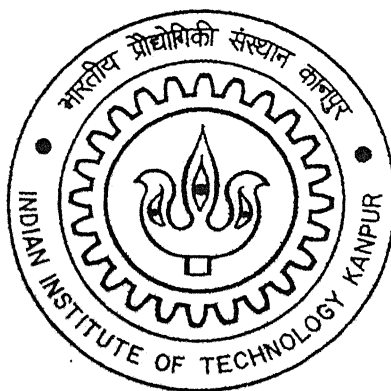# Synthesis And Characterization
Of
Titanocene Catalysts, Cocatalysts And Polyethylene

Thesis submitted
in partial fulfilment of the requirements
for the Degree of

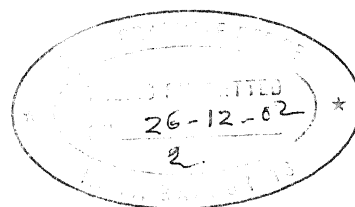*Master of Technology*

By

Vimal Katiyar

to the

Department of Chemical Engineering

INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

December 2002

Certificate

This is to certify that the work contained in the thesis entitled

"Synthesis And Characterization Of Titanocene Catalysts, Cocatalysts And Polyethylene" has been carried out by **Vimal Katiyar** under my supervision and it

has not been submitted elsewhere for a degree.

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Abstract

The synthesis of Bis- (cyclopentadienyl) titanium dichloride (Titanoene Catalyst) has been performed. Red coloured crystalline form of Cp_2TiCl_2 having a melting point of 285^0C is obtained. Infrared and Nuclear Magnetic Resonance Spectras show that the structure of Cp_2TiCl_2 matches with the reported values in the literature. During the synthesis of Tri Ethyl Aluminum (TEAL), impurity of diethyl ether has been traced. TEAL is highly hygroscopic and pyrophoric in nature and gives a boiling point of 110^0C at 25 mm Hg. NMR spectra proves the presence of ether in TEAL. Ethyl Aluminoxane (EAO) has been synthesized by two methods. Hydrated Aluminum Sulphate is used as water source in first method and etheral water in second. In IR spectra, characteristic peak of Al-O-Al is observed at 802 cm^{-1}. X- Ray diffraction pattern shows amorphous nature of EAO. Several synthesis runs have been performed for Titanocene catalyst and cocatalyst -TEAL & EAO. With the help of above synthesized catalyst and cocatalysts, two sets of catalyst combinations has been made. One set contains $TiCl_4$ / TEAL and $ZrCl_4$ /TEAL for Ziegler – Natta based polymerization. The second set having unsupported Cp_2TiCl_2 / TEAL / EAO and silica –alumina supported Cp_2TiCl_2 / TEAL / EAO have been utilized for Metallocene based polymerization. Polymerization of ethylene has been successful using both sets of catalyst combinations, however silica-alumina supported metallocene polymerization failed. Characterization of polyethylene such as IR spectra, CHN analysis, and differential scanning calorimetry analysis has been performed which proves that catalyst combination is suitable for polymerization of ethylene. Activity of $TiCl_4$ / TEAL catalyst increases with increase in Al /Ti molar ratio and reaches an asymptotic value at Al / Ti molar ratio of 200. Activity of $TiCl_4$ has been found greater than $ZrCl_4$. It was noticed that polymerization of ethylene has been successful using unsupported metallocene catalyst when Al / Ti molar ratio reaches 1250.

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CHAPTER 1

INTRODUCTION

Polyethylene is nothing more than a long chain of carbon atoms, with two hydrogen atoms attached to each carbon atom and represented by simplest formula $[-CH_2-CH_2-]_n$ [1]. It is a very commonly used polymer and was first produced in England by ICI in 1933 by polymerizing the ethylene monomer (B.P.-104°C).Initially the polyethylene was produced by the high pressure polymerization of ethylene, using oxygen as the initiator. The reaction occurs at a pressure as high as approximately1500 atm. and in the temperature range of 180° – 250°C. It is interesting to note that even an extremely small quantity of oxygen say, 0.1% was sufficient to initiate the polymerization.. Apart from oxygen, other initiators include peroxides, hydroperoxides and azocompounds. Polyethylene produced by this process has a low density, around 0.91 to 0.92 g/cc, because of branching; it was identified as a low-density polyethylene (LDPE) while practically no solvent dissolves it at room temperature. Several solvents like Carbon Tetrachloride, Toluene, Xylene, decaline can dissolve PE at high temperature [2].

Branched polyethylene (LDPE) is often made by free radical vinyl polymerization. Linear High Density Polyethylene (HDPE) is made by a more complicated procedure called Ziegler-Natta Polymerization. But Ziegler-Natta polymerization can be used to make LDPE, too [3]. By co-polymerizing ethylene monomer with an alkyl-branched comonomer as one gets a copolymer which has short hydrocarbon branches. Copolymers like this are called linear low-density polyethylene or LLDPE, using a comonomer with the name 4-methyl-1-pentene, High-density polyethylene (HDPE) was produced by the coordination polymerization of the monomer using tri alkyl aluminium and titanium tetrachloride as a catalyst [4]. This catalyst is known as Zieglar Natta catalyst. Because of this catalyst, the polymerization was carried out at low pressure and polymer possesses densities as high as 0.965 gm/cc, which is more than the density of LDPE. It has a melting point of 144 to 150°C. It is much stiffer than LDPE and has high tensile strength and hardness. Chemically it is more resistant than LDPE and has significantly lower gas permeability [5]. The density of polyethylene decreases with an increase in branch number and decreases with an increase in molecular weight. Hence any physical property related to crystallinity such as stiffness, density and yield stress have been affected by branching and chemical composition.
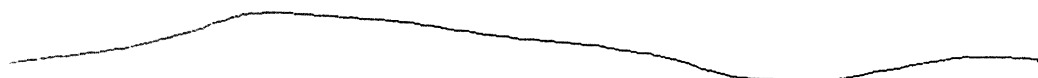
A molecule of linear polyethylene, or HDPE

A molecule of branched polyethylene, or LDPE

1.1. ZIEGLER- NATTA CATALYST

The Ziegler-Natta catalyst was discovered in the laboratories of Ziegler in the fall of 1953 and Natta in spring of 1954. The Ziegler school revealed that high density polyethylene was easily made at low pressure with binary mixture of metal alkyl of group I to III and transition metal salt of group IV to VIII, such as $AlEt_3$ to + $TiCl_4$ [6]. The Natta school then demonstrated the ability of the same catalyst and to a greater extent, catalyst containing lower valent transition metal chloride such as $TiCl_3$, to form isotectic polymers from α-olefins. The Ziegler Natta catalyst has now joined ranks of conventional initiators as one of the major methods that we have to initiate the polymerization. The versatility of this catalyst is the outcome of its inherent sensitivity to a number of factors that influence its kinetic and stereochemical behaviour, which has provided a powerful handle by which scientists can modify the behaviour of the catalyst. Several important factors have been identified:

(a) Metal alkyl structure –choice of metal and nature of ligands.

(b) Transition metal structure-choice of metal, nature of ligands, crystal structure, valency & (c) the way, the components are brought together and used in polymerization- absolute and relative concentration, temperature, pressure and time [7].

However, Ziegler-Natta catalysts are unable to add interlinking side chains that improve durability and are not too stereospecific for polypropylene.

1.2. CHEMISTRY OF ZIEGLER-NATTA CATALYST

How the Ziegler-Natta catalyst works to make polymers, is explained by using $TiCl_3$ and $(C_2H_5)_2ClAl$ (DEAC) catalyst. $TiCl_3$ can arrange itself into a number of crystal structures. It looks something like this:
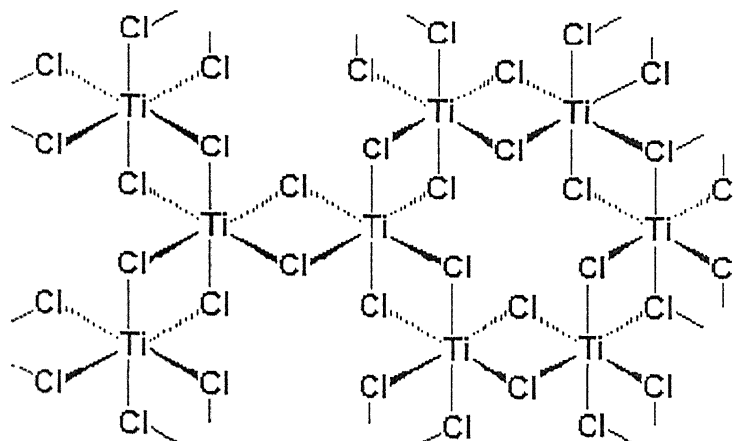
a crystal of $TiCl_3$

As we can see, each titanium atom is co-ordinated to six chlorine atoms, with octahedral geometry, In the interior of the crystal, each where titanium is surrounded by six chlorines but at the surface of the crystal titanium atom is surrounded by five chlorine atoms, and on the other side by empty space [8].
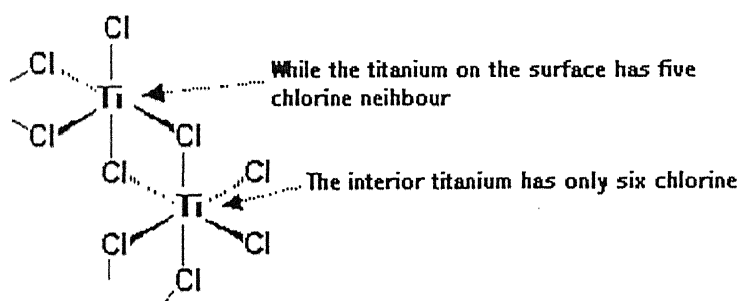
This type of atomic arrangement of $TiCl_3$ shows chlorine shortage on the surface of the transition metals, as we know that it has six empty orbitals (resulting from one $4s$ and five $3d$-orbitals) in the outermost shells. So the titanium has to be co-ordinated with enough atoms to put two electrons in each of the orbitals. The titanium atom on the surface of the crystal has enough neighbour atoms to fill five of the six orbital and one orbital is vacant as an empty orbital, shown as an empty square in the picture.
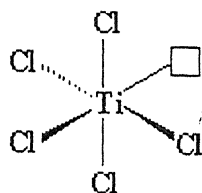
A surface titanium has an empty orbital.

The titanium behaves just like an electrophile and wants to fill its empty orbital. Hence the $(C_2H_5)_2ClAl$ donates one of its ethyl groups to the electron deficient titanium along with transfer of lone pair electron. During this process $(C_2H_5)_2ClAl$ has extracted one chlorine atom from Ti. We still have an empty orbital [9].
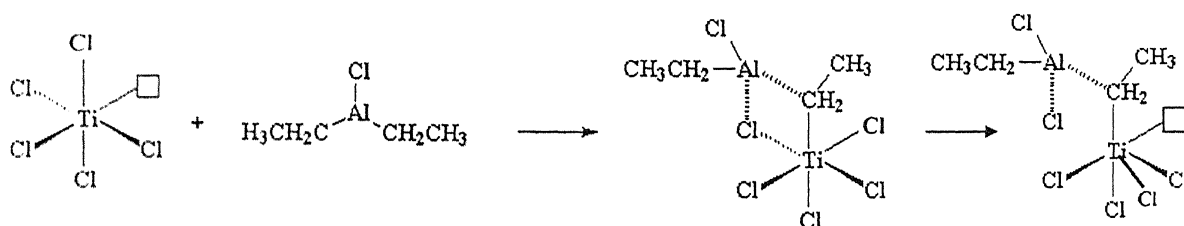
This process forms the active polymerization catalyst, which happens to be insoluble (unlike the 2 components that make up the complex), commonly known as heterogeneous catalyst. Then vinyl monomer like propylene comes in contact with catalyst and transfers the two π electrons. These electrons can be used to fill the empty orbital of the titanium. The propylene and the titanium form a complex, which is represented like this:
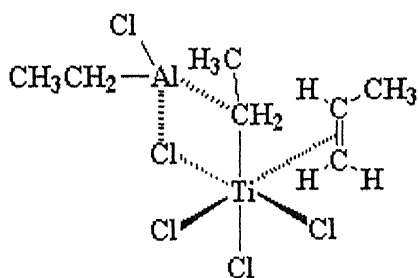
The π-electrons from propylene end
up filling titanium's empty orbital.

The catalyst gives essentially a mixture of atactic and isotactic polymer [10]. As the catalysts developed, much higher activity ensured. Still, however, a substantial amount of atactic material was produced, which had to be lowered by the addition of a Lewis base (like esters or ethers).

1.3. METALLOCENE CATALYST

As early as 1957 Natta reported the polymerization of ethylene with the titanocene catalyst Cp_2TiCl_2 and the cocatalyst triethyl aluminum, a cocatalyst traditionally used in Ziegler-Natta olefin polymerization systems. Metallocene is a catalyst for making polyethylene and polypropylene. Metallocene is the single most important development in catalyst technology since the discovery of Ziegler-Natta catalysts. The term metallocene was used to describe a complex with a metal sandwiched between two-cyclopentadienyl (Cp) ligands, including those with substituted Cp rings, or those with bent sandwich structures, and even the half-sandwich or mono-Cp complexes [11].
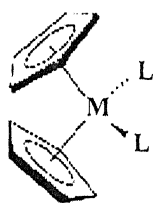
[M = Transition Metal (Zr, Ti, Hf), L = Ligands (Cl or CH_3 or mixture of Cl and CH_3)]

Just like the Ziegler-Natta catalyst, metallocene contains a metal atom that attacks carbon-carbon double bond, allowing vacancy to electronically bond to another monomer. The original catalyst consisted of Titanium or Zirconium linked to two five-carbon (usually each carbon attached to a hydrogen atom) rings and to two other groups. The two rings enclose the metal atom like a half-open clamshell. Electrons associated with rings influence the metal, modifying its propensity to attack carbon-carbon double bonds. This catalyzes the production of polyethylene with the control of chain size by adding more or less electron donating group even under the presence of larger molecules. Dow Chemical has adopted a modification of added silicon joining the two five-carbon rings on one side and replacing one of the five-carbon ring atom with a nitrogen. (π-$C_5H_5)_2Zr(NMe_2)_2$The reaction run under 120 degrees Celsius or more, which rapidly produced polyethylene with the controlled amount of interlinking chains. The second modification consists of a Titanium atom linked to two five-carbon rings, which is bridged by a two-carbon linkage, and organic groups attached to rings that it gives symmetry of a playing card. This allows the catalyst to back-skip which results in the isotactic conformation of polypropylene [12]. The third modification consisted of two

six-carbon rings attached on to each side of one of the five-carbon rings, which created a mirror image.

This allows the catalyst to migrate down the chain resulting in a syndiotactic conformation. With metallocene catalyst, polyethylene is more resistant to tearing and polypropylene is harder, more crystalline, and more transparent along with other advantages over the conventional catalyst. The activity of the metallocene with the Ziegler-Natta cocatalyst was very low and therefore showed little commercial promise.

The current interest in metallocenes originated with a discovery by Kaminsky at the University of Hamburg in 1967[13]. While studying a homogenous $Cp_2ZrCl_2/Al(CH_3)_3$ polymerization system, water was accidentally introduced into the reactor leading to an extremely active ethylene polymerization system. Subsequent studies revealed that the high activity was due to the formation of methylaluminoxane (MAO) as a result of the hydrolysis of the trimethyl aluminum, $Al(CH_3)_3$. Aluminoxanes have been subsequently used as cocatalyst. It is because of the discovery of this co-catalyst in Kaminsky's lab that metallocene with aluminoxanes are also commonly called "Kaminsky" catalysts, Kaminsky and his coworkers also noticed that the addition of water to the trialkyl aluminium in a molar ratio of 1:1 significantly improves the catalyst activity [14].
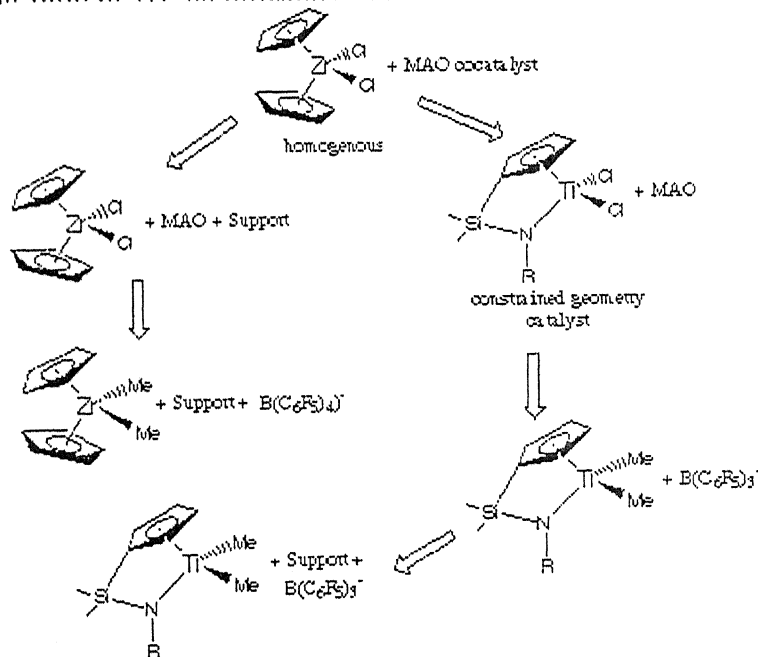
Figure 1.1 . The evolution of metallocene olefin polymerization catalysts.

1.4. ZIEGLER NATTA Vs METALLOCENE BASED CATALYSTS

The metallocene catalysts are generally called single site catalyst because of the equality of each catalyst site, but the conventional Ziegler-Natta catalysts are multiple sites. Compared to conventional Zieglar-Natta catalyst, metallocene catalysts are characterized by higher activity, narrow molecular weight distribution, uniform comonomer incorporation, outstanding ability to incorporate sterically demanding comonomers, narrow comonomer distribution. From an ecological viewpoint, the total ash arising from the incineration of metallocene polymer is 20 ppm compared to 330 ppm for the equivalent Ziegler-Natta polymer [15,16].

Table 1.1: Comparison between Ziegler Natta and Metallocene Catalysts

Characteristics	Ziegler Natta	Metallocene
Catalyst		
Catalyst sites	Multiple	Single
Cocatalyst	Simple Aluminium Alkyl	Alkyl aluminoxane and bulkyanions
Electron donor	Both internal & external needed	Not needed
Polymer		
MWD	Broad	Narrow
Chainlength	Nonuniform	Uniform
Bulk density	High	Low
Melting Point	Independent of polymerization temperature	Dependent on polymerization temperature
Soluble Content	High	Low

A look at Table 1.1 indicate that metallocene catalyst system possesses an extraordinary versatility for the polymerization of a variety of monomers[17, 18].

1.5. POLYMERIZATION OF OLEFINS USING METALLOCENE CATALYST

Polymerization mechanism of metallocene alongwith Aluminoxane (RAO) and/or alkyl Aluminium proceeds via alkylation of the metallocene which generates the active site. The active species is believed to be a 14 valence electron alkylmetallocenium $[Cp_2MR]^+$ cation and $[(RAO)R]^-$ anion:

$$Cp_2M \begin{array}{c} Cl \\ Cl \end{array} \xrightarrow{RAO} Cp_2M \begin{array}{c} R \\ Cl \end{array} \xrightarrow{RAO} Cp_2M \begin{array}{c} R \\ R \end{array}$$

$$Cp_2M \begin{array}{c} R \\ R \end{array} \rightleftharpoons Cp_2M \begin{array}{c} R \\ R \end{array} Al \ RAO \rightleftharpoons Cp_2M^{\oplus} \begin{array}{c} R \end{array} + [R \ Al(RAO)]^-$$
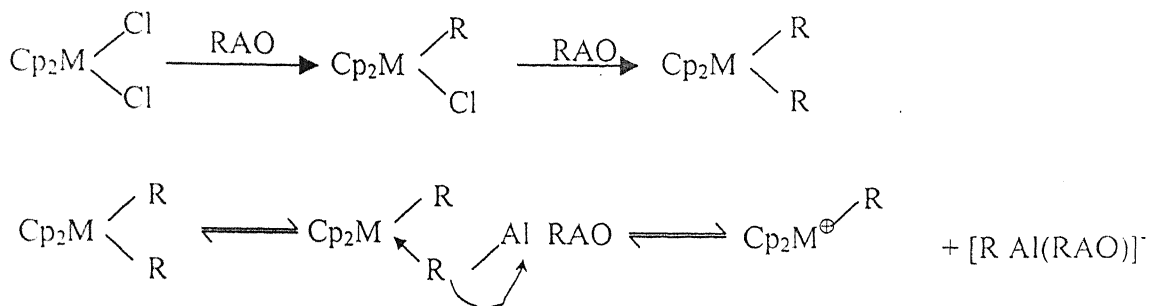
Alkylmetallocenium cations can be detected by electrodialysis[19], because in presence of electric field cations can be observed by their migration.The incoming monomer [H$_2$C=CHR] coordinates with the cationic alkylmetallocenium ion [Cp2MR]$^+$ and is inserted, via metal carbon bond [Cp$_2$MR-CH$_2$-CHR]$^+$.Now monomer migrates through the four center transitional state as the growing chain, and each successive monomer unit is similarly added to the growing polymer chain[Cp$_2$MR-H$_2$C-CHR-polymer chain]$^+$ regenerating the vacant coordinate site for next incoming monomer[23,24].
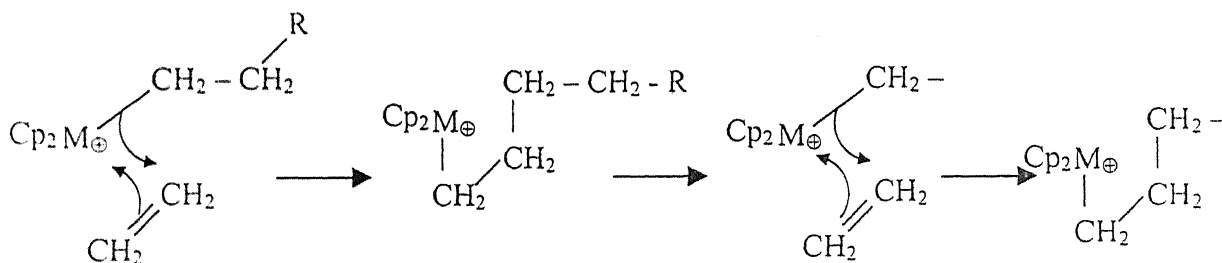
Now depending on the metallocene catalyst, the cocatalyst, and the reaction conditions, the growing polymer chain can be terminated either by

(a) β-hydride elimination [25,26],

$$Cp_2M^{\oplus} \begin{array}{c} CH_2 \\ CH-R \\ H \end{array} \longrightarrow \begin{array}{c} CH_2 = CH - R \\ + \\ Cp_2M^{\oplus} - H \end{array}$$
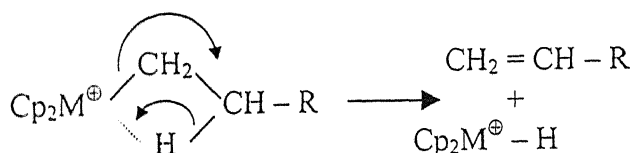
(b) By Hydrogenation [27,28]

$$Cp_2M^{\oplus} \begin{array}{c} CH_2 - CH_2 - R \\ H \\ H \end{array} \longrightarrow Cp_2M^{\oplus} - H + CH_3 - CH_2 - R$$
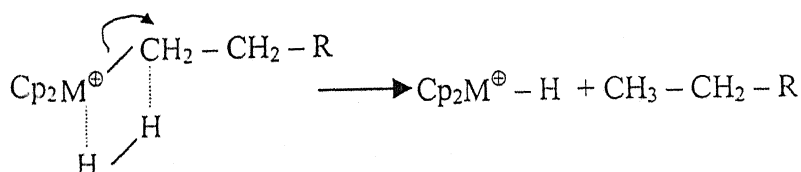
(c) By Chain transfer to the monomer or hydrogen [29,30]
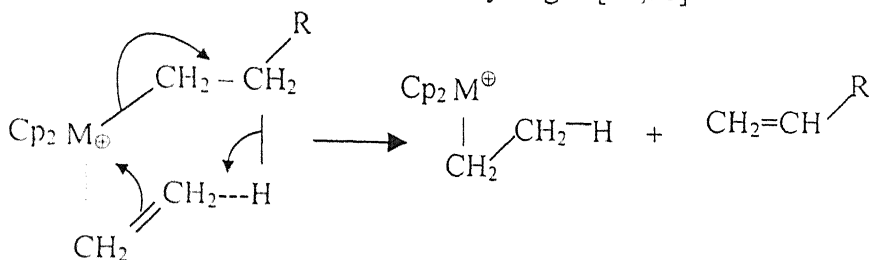
M = transition Metal (M = Zr, Ti, Hf)

Unlike the conventional heterogeneous Ziegler-Natta catalyst system, the metallocene catalyst system has the advantage of producing polyethylenes having terminal unsaturation, which could be used for building functionalities in the polymer. Also hydrogen could be used for controlling the molecular weight and the corresponding polydispersity index of the metallocene based polyolefins (30-32). During the polymerization the calculated use of hydrogen is necessary [33,34].

1.6. POLYMERIZATION PROCESSES

Polymerization of Olefins (ethylene, propylene etc.), using above mentioned catalyst has been studied in solution phase, slurry phase and gas phase process. Depending on a number of factors, such as the structure of the polymer, nature of the solvent, and temperature of polymerization, the polymer may be formed in one of several physical states: (1) in solution phase (the solution process); (2) In the form of solid particles suspended in a liquid solvent (the slurry process); (3) in the form of solid particles in a fluidized bed (gas phase process). These three conditions form the basis of the three main types of processes that can be used for commercial production of olefin and diolefin polymers. Each process has led to a commercial application with its own advantage for a particular monomer-polymer catalyst system. These processes can be done in a batch or a continuous operation. In the batch operation, polymerization takes place in the reactor for a specific time and then the entire polymer is removed and isolated. In a continuous process, on the other hand, some polymer is continuously removed while fresh catalyst and olefin are simultaneously added. Processes possessing features of both are possible. Because of its simplicity, the batch operation is mostly used in the small laboratory synthesis.

1.6.1. SOLUTION PHASE POLYMERIZATION

In a solution phase polymerization process, the polymer is dissolved throughout the polymerization. The catalyst, however, may be soluble or insoluble in the reaction medium. The conditions for maintaining the polymer in solution depend on the structure of the polymer, the reaction solvent, and the temperature of polymerization. For example, poly-cis-1, 4-butadiene and poly-cis-1, 4-polyisoprene remains in solution at room temperature when the solvent is benzene. Poly-α-olefins containing long pendant groups, such as 1-octene, are soluble in aromatic and aliphatic solvents at ambient temperatures. Hoeg and Liebman [35] characterise the solution polymerization of propylene in cyclohexane at temperature between 120^0C using the AlR_3 –$TiCl_3$ catalyst. Solution phase polymerization for production of high-density polyethylene has several advantages. One is better control over molecular weight and molecular weight distribution. Products that have low molecular weights and narrow molecular weight distributions have been easily made. These products are best suited for use as injection molding grade polyethylenes [7].

1.6.2 SLURRY PHASE POLYMERIZATION

In slurry phase almost all of the polymer separates as a separate phase from the reaction solvent, which can be an aliphatic or aromatic solvent or even the monomer itself. The slurry process has found wide use for the synthesis of polyolefins but not polydienes. The polymer particles can vary in size, shape and density. Soluble and colloidal catalysts produce a polyethylene that has a flocculant, gelatinous appearance in the reaction solvent. Only a limited amount of polymer, about 3 to 6 wt%, is present in the reaction mixture. In comparison, if heterogeneous catalysts are used, slurries containing 10 to 40 wt% polymers in the solvent can be achieved. The throughput of polymer (for example, polyethylene, polypropylene, or poly1-butene) in a reactor is increased as the slurry concentration is increased. The slurry process has most often been used for laboratory investigations of Ziegler-Natta & Metallocene catalysts and for synthesis of polyolefins. Usually temperature in the range of 25^0 to 100^0C are used, but the upper temperature depends on the polymer and solvent; for example, for isotactic poly-1-butene, it is about 50^0C using $(Et)_3$ Al – $TiCl_3$ in heptane [8].

Slurry processes are better suited for production of high molecular weight materials for use of extrusion and blow molding grades .In recent years very highly active slurry processes have been developed that use supported titanium catalyst.

These polymerizations are done between 30^0 to 90^0 C and at 100 to 500 psig ethylene pressures. Between 100 to 500 kg polymer is obtained per gram of titanium used. The residual titanium ash is so low that its removal is not required

Selected examples of supported catalyst – polymerization of ethylene using slurry phase polymerization from the patents.

1. Silica supported $Cp_2\ ZrCl_2$/ MAO + $(CH_3)_3Al$ cocatalyst for ethylene polymerization [36].

2. Silica supported $Cp_2\ ZrCl_2$/ MAO + $(CH_3)_2ClAl$ cocatalyst for ethylene polymerization[36].

3. Magnesium chloride supported $TiCl_4$ / TEAL (tri ethyl aluminium) for ethylene polymerization [37].

4. Silica supported bis (tetra hydro indenyl) Zirconium dichloride/ MAO for ethylene polymerization [38].

1.6.3 GAS PHASE POLYMERIZATION

The distinguishing characteristic of gas phase polymerization is that the system does not involve any liquid phase in the polymerization zone. Polymerization does occur at the interface between the solid catalyst and the polymer matrix, which is swollen with monomers during polymerization. The gas phase plays a role in the supply of monomers, mixing of polymer particles, and removal of reaction heat. Hence, the gas phase polymerization is also called dry polymerization. In this process, polymer particles are passed downward in the reactor and monomer mixed with diluents gas is passed counter currently upward in the reactor through a series of vertical fluidized bed reaction zones. The reaction zones can be controlled independently by taking off-gas from the last reaction zone, cooling it, and recycling portions of such off-gas to each of the reaction zones [39]. The first commercial gas phase polymerization plant using a fluidised bed reactor was constructed by Union Carbide in 1968 at Seadrift. This process was developed initially for HDPE (High Density Polyethylene) production [40]. Schmid and co-workers also made ethylene Polymerization at 6 atm and 50^0C in presence of Al (IsoBu)$_3$ [TIBA]-TiCl$_3$ Catalyst; 20 part of ethylene and 0.019 parts of catalyst were supplied to the reactor per hour. The polyethylene product had a molecular weight of 1,00,000 and ash content of 0.12%. Polypropylene was similarly polymerized with an Al(Et)$_3$ [TEAL]– TiCl$_3$ catalyst [41].

For polymerization of ethylene in gas phase using CH_3TiCl_3-$TiCl_3$ catalyst, Edgecomble [42] found only the initial rate to be first order. Activation energy for polymerization was 10 kcal/mole. Compared with slurry and solution processes, however, gas phase processes do have the following disadvantages [8]:

- The poor heat transfer efficiency of the gas phase is a disadvantage. Hence additional inert heat transfer agent is required to maintain stable reactor operating condition at high production rate.

- There is a possibility of sintering and agglomeration of the polymer particles due to the formation of local hot spots when a high activity catalyst is used.

- Reactor operating temperature is limited to the raisin softening point. Thus the productivity of catalyst is also limited.

1.7. METALLOCENE-BASEDPOLYETHYLEN CHARACTERISTICS

Metallocene-based catalysts have distinct kinetic characteristics for polyethylene polymerizations, which are summarized as follows:

1.7.1. Super high productivity and good polymerization

Polymerization rate reaches a maximum within 5 min, decays slightly, and then remains almost constant. For the Cp_2MR_2 (M= Ti, Zr, Hf; R = Cl, CH3) catalyst family, zirconium catalysts are more active than titanium or hafnium systems, at temperatures over 50^0C. The co-catalyst methylaluminoxane is better suited then ethylaluminoxane or isobutylauminoxane [43-45].For $Et(Ind)_2MCl_2$ (M= Zr, Hf), Hf catalysts show higher activities [46]. Productivity of metallocene catalysts can be up to $3x10^7$gm of PE/ (g of Zr-h) [47].

1.7.2. Very high initiation efficiency

Active center concentration is 75-100% of Zr for ethylene polymerization using ziroconocene/MAO, increase monotonically, with temperature, and is sensitive to Al/Zr ratio. [45,48,49]. Similar behaviour exists for titenocene.

1.7.3. Narrow molecular weight distribution

In general polydispersity of PE or its copolymers produced using metallocene catalysts is between 2 and 5; in most cases, polydispersity is about 2[50]. Polydispersity can be controlled by mixing metallocene catalysts or by mixing metallocene with heterogeneous Ziegler-Natta catalysts [46,51].

1.7.4. Molecular weight sensitivity to hydrogen and temperature

Chain transfer to hydrogen and β-hydride elimination rate constants are 2-3 orders of magnitude greater than the corresponding values found the $MgCl_2$ supported heterogeneous Ziegler-Natta catalysts [52]. Hydrogen also reduces polymerization rate [46,53].

1.7.5 Uniform incorporation of co-monomers

Composition of copolymer is almost the same as the monomer feed composition, and co-monomer is uniformly distributed in copolymer chains regardless of chain length [49,54]. The effect of co-monomer on ethylene polymerization rate depends on polymerization temperature. 1-hexene or propylene enhances ethylene consumption rate at 30 and 60°C. However, 1-hexane reduces ethylene polymerization rate at 70 and 95°C [55].

1.7.6. Stereo-chemical control in microstructure of olefin polymers

Metallocene catalysts by manipulating the structures of organocompounds can polymerize olefins with very high stereo regulatory to give either isotactic or syndiotatic polymers [49].

1.7.7. Very high co-catalysts ratio

To obtain high polymerization rate and high active centre concentration, the Al/Zr, ratio needs to be 10^3-10^4 or higher [45,50]. If the Al/Zr ratio is small, the polymerization rate increases slowly and has an induction period [56]. The reason for high co-catalyst ratio is still unclear. The cost of co-catalyst ratio could be more than 200-300 times the cost of the catalyst in commercial production. Hence, high co-catalyst ratio is one of the major barriers to commercialization of metallocene technologies.

1.8 Polymer Particle Morphology Development

One of the most important features of ethylene polymerization using heterogeneous catalysts is replication of polymer particles [57]. This suggests that the morphology development of polymer particles depends on the original morphology of the catalysts. Polymer growth on titanium crystal surfaces has been carefully examined using electron microscopy [58] and it was found that the polymer first accumulates on boundaries of catalyst fragments and at existing cracks [59]. The shape of the polymer growth was usually governed by that of the active catalyst particles. The morphology if classical Ziegler-Natta catalyst was determined using electron scanning microscopy. The gross catalyst particles are composed of primary particles whose size and shape depend on the

preparation conditions of the catalyst. The size of a primary particle is in the range 10-1000°A in diameter. The shape and reactivity of primary catalyst crystals are responsible for the fiber like structures that make up the final polymer particles. On the basis of electron microscopy and adsorption data, Bukatova [60] suggested that the 10-30μm catalyst granules consist of three levels of particles: 200-1000Å. 1000-5000-Å, and <5μm particles. The size of catalysts particle in the final polymer matrix is in the range of 200 to 500 Å. Mkrtchyan *et al.* [61] used microspherical mesoporous copolymers of styrene and divinylbenzene as a catalyst support, and found that the microspheres of supported catalyst also dispersed in the polyethylene matrix.

The morphology replication nature of ethylene polymerization provides a guideline for catalyst development [62]. Polymer morphology control can be considered in the catalyst preparation stage. Although the reactivity and chemical composition of $MgCl_2$ or silica supported catalyst is different from those of a conventional Ziegler-Natta catalyst, the morphological replication nature of ethylene polymerization using the supported catalyst is the same. The morphology of a final polymer particle is governed by the morphology of the supported catalyst. However, for supported catalysts, the primary particle is the support material, e.g., $MgCl_2$ crystal or silica. It has been experimentally observed that polymer grows on the edges of $MgCl_2$ crystals treated with $TiCl_4$ and activated by $AlEt_3$ [63]. Polymer morphology development using supported catalysts has been examined in many laboratories. All the evidence shows that the polymer particle size and shape replicate its parent catalyst size and shape). The $MgCl_2$ particle and/or silica surface favours the most isotropic distribution of $TiCl_4$ active centres [64]. Figure shows the replication relationship between silica supported catalyst and polymer particles made with the catalyst [65].
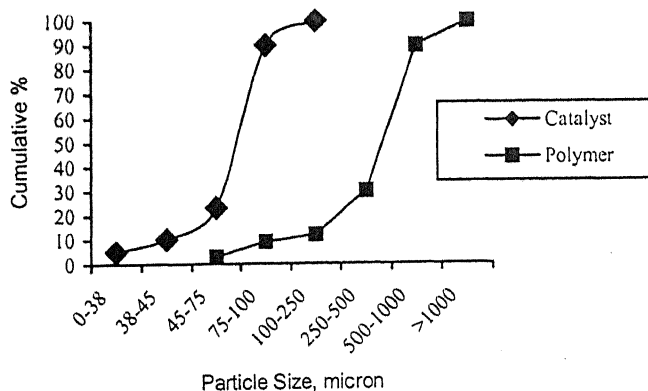
Fig. 1.2 Particle size replication of ethylene polymerization with silica-supported Ziegler-Natta catalyst

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CHAPTER 2

Synthesis and Characterization
of
Bis (η-Cyclopentadienyl) Titanium dicloride

2.1 Theoretical Background

Metallocenes are relatively old organometallic complexes that were discovered as early as 1951. First compound discovered was ferrocene, a simple complex consisting of an iron center and two cyclopentadienyl (Cp) rings surrounding the metal. Ferrocene was first prepared by reacting cyclopentadienyl-magnesium bromide with ferric chloride in diethyl ether/benzene solution [1].
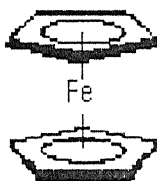
Ferrocene

The term metallocene was used to describe any complexes like 1 & 2 with a metal center and Cp ligands surrounding it. Presently, the term is used to describe a wide variety of organometallic complexes including those with altered structures such as substituted Cp rings and bridging atoms as in 3.
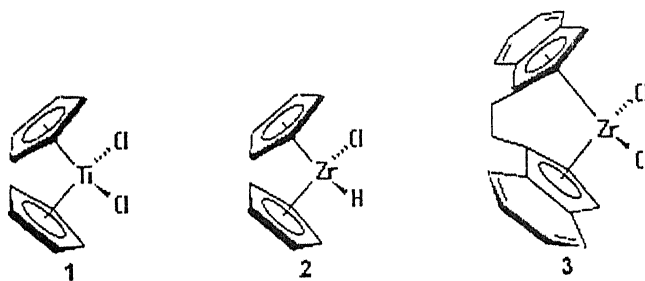
2.1.1 Representative Examples of Metallocenes [2,3]

(a)   Non-stereorigid metallocenes

1. Cp_2MCl_2 (M = Ti, Zr, Hf)

2. Cp_2ZrR_2 (R = Me, C_6H_5, CH_2Ph, CH_2SiMe_3)

3. $(Ind)_2ZrMe_2$ (Me = CH_3)

(b)   Nonstereorigid ring-substituted metallocenes

1. $(Me_5C_5)_2MCl_2$ (M = Ti, Zr, Hf)

2. $(Me_3SiCp)_2ZrCl_2$

(c)   Stereorigid metallocenes

1. $Et(Ind)_2ZrCl_2$

2. $Et(Ind)_2ZrMe_2$

3. $Et(Ind\ H_4)_2ZrCl_2$

(d)   Cationic metallocenes

1. $Cp_2MR(L)^+ [BPh_4]^-$ (M = Ti, Zr)

2. $[Cp_2ZrMe]^+ [C_2B_9H_{11})_2M]^-$ (M = Co)

(e)   Supported metallocenes

1. $Al_2O_3 - Et[Ind\ H_4]_2ZrCl_2$

2. $MgCl_2.Cp_2ZrCl_2$

3. $SiO_2.Et[Ind]_2ZrCl_2$

2.1.2 Bis (η - Cyclopentadienyl) titanium Complexes

The carbonyl complexes of the group IV B metals have received a lot of attention because they are assumed to provide a convenience source of the carbinoid unit " $(C_5H_5)_2Ti$" [4]. These complexes are well characterized, stable, and relatively easy to synthesize. Few of them are given below:

2.1.2a. Titanocene

Titanocene is dark green, diamagnetic, air sensitive solid, which is formed by the reaction of $TiCl_4$ with Cyclopentadienyl sodium.[5]
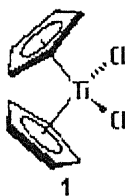
Titenocene(4)   Cyclopentadienyl titanium dichloride(1)

2.1.2b. Bis (η - Cyclopentadienyl) titanium chloride:

$TiCl_3$ was suspended in 300 ml of tetrahydrofuran in a flask. The suspension was magnetically stirred and solid TlCp was added over, it a rapidly dissolved to give a green brown solution of bis(cyclopentadienyl) titanium chloride having melting point of 285-288^{0}C [6]. The spectra of the four Cp_2TiX (X= F, Cl, Br, I) metal to halogen stretching frequencies fall below 600 cm^{-1}.

2.1.2c. Bis (η - Cyclopentadienyl) titanium dichloride

Bis(Cyclopentadienyl) titanium difloride is coloured green; dichloride; green brown; dibromide is red brown and diIodide is black. On exposure to air all are oxidised to yellow– orange solids though the fluoride tends to show a decreased sensitivity towards oxygen. All are soluble in air free water, in THF, and in benzene although the dissolution of the fluoride is very less soluble in organic solvent. In the IR spectra of Cp_2TiCl_2 to metal- ring tilting vibration assigned a weak peak at 820 cm^{-1}; Generally the spectra of all four members of the series was strong band at 820 ± 3 cm^{-1} [6].

2.1.2d. μ - (η^5 : η^5-Fulvalene) - μ dihydridobis (η- dicyclopentadienyltitanium)

[(C$_2$H$_5$) (C$_5$H$_4$)TiH]$_2$ (5)

Anhydride can be conventionally prepared by reaction of one mole cyclopentadienyl titanium dichloride with 2 mole of sodium naphthalene in tetrahydrofuran at room temperature. It is extremely air sensitive. The compound is characterized by an intense metal- hydride streching frequency which appeared at 1230 cm^{-1}[7]. Whereas hydrogenolysis of (η-C$_5$H$_5$)$_2$Ti(CH$_3$)$_2$ solution at room temperature yields mainly hydride (5), but the reaction of (η-C$_5$H$_5$)$_2$Ti(CH$_3$)$_2$ solution with hydrogen gives a purple complex characterized as the bridging hydride (6).
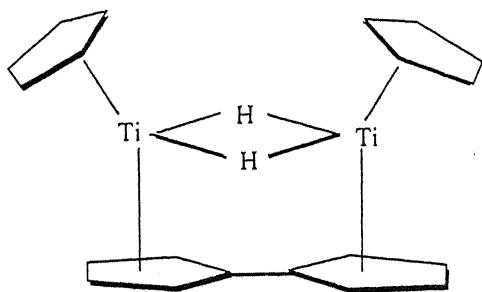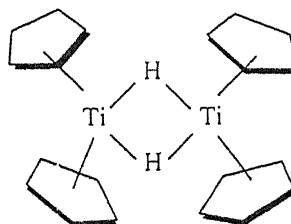
(5)   (6)

2.2. General Methods of Preparation of Bis-Cyclopentadienyl Metal Dihalide [8]

Bis-cyclopentadienyl dihalides of metal (Ti, Zr, Hf) were made by the reaction of cyclopentadienylmagnesium chloride or bromide with the metal halide (Cl, Br), in benzene and ether solution respectively. But the more convenient procedure which gives higher yield of cyclopentadienyl metal dihalide was produced by the reaction of cyclopentadienylsodium with the metal halide in tetrahydrofuran solution. cyclopentadienylsodium was prepared by adding the theoretical amount of cyclopentadiene to finely divided sodium in tetrahydrofuran .The mixture was stirred at room temperature until gas evolution ceased; the resulting orange solution was cooled and was run slowly into the solvent plus the metal halide, with rapid stirring and ice cooling.

The procedure employed for isolation of the bis-cyclopentdienyl metal dihalide was very similar in all cases. After stirring the reaction mixture for 2-3 hours, the solvent was removed under reduced pressure. The residue was then repeatedly extracted with boiling chloroform through which was passed a slow stream of hydrogen chloride. The extract was evaporated and the residue re-extracted with chloroform saturated with hydrogen chloride. For bis-cyclopentadienyltitanium (IV) chloride and bromide, the product was crystallized from toluene. For the bis-cyclopentadienyl halides of zirconium, vanadium, niobium and tantalum, the chloroform extract, after saturation with the appropriate hydrogen halide, was cooled in a dry ice- acetone bath and the crystals separated by rapid filtration. Bis cyclopentadienylzirconium (IV) bromide was re-crystallized from carbon tetradienyl halides of vanadium, niobium and tantalum were re-chloride or bromide, by cooling the solutions of -70^{0}C.

An alternative procedure for the isolation of the bis-cyclopentadienylniobium and tantalum bromides was to pour the reaction mixture into an ice slush of 6N hydrobromic acid. The yellow aqueous phase, which contained bis-cyclopentadienylmetal hydroxy ions was treated with bromine water. The resulting yellow precipitate was centrifuged, washed with 1 N hydrobromic acid until free from magnesium or sodium salts, and dissolved in boiling 48% hydrobromic acid. This solution was distilled azeotropically with benzene in stream of hydrogen bromide; after removal of excess benzene, the product was crystallized from chloroform as before.

2.3. Variation of π-Ligands

The catalyst activity, stereospecificity, comonomer incorporation capability, and the resulting polymer molecular weight characteristics are also dependent on the cyclic π-

ligands [9,10]. The titanocene based on indenyl, (Ind)₂TiMe₂, showed remarkably higher activity than the corresponding titanocene based on Cp that is Cp₂TiMe₂. Although the activity was solvent-dependent, the indenyl ligand complexes are more active in toluene than in heptane [11]. The overall effects of changing the π-ligand on the activity of the chloride free titanocene catalyst systems are in order of (Ind)₂ > Cp₂. On replacing the Cp with (neomethyl-η^5-cyclopentadienyl) and testing the resulting (n-MeCp)₂TiCl₂/MAO system, the polymerization rate, catalyst induction period, and catalyst deactivation were affected owing to the electronic and steric effects [12]. Single alkyl substituents on each Cp increases polyethylene formation possibly because of electron donation enhancement of the coordinated anionic propagation. The substituent size effects are opposite, similar results have been obtained by different investigators [13-17]. The use of other substitutents decreased the catalytic activity of co-polymerizing ethylene and hexene-1 in the order of
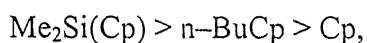
$$Me_2Si(Cp) > n-BuCp > Cp,$$

This is also explainable in terms of electronic effect. However, the weight-average molecular weight decreased [18] in the order of n-BuCp > Cp > Me₂Si(Cp).

Comparison of the (MeCp)₂TiCl₂, (EtCp)₂TiCl₂, (Me₅Cp)₂TiCl₂, (Me₅Cp)CpTiCl₂ and (NmCp)₂ TiCl₂ (Nm = neomethyl) Catalysts shows that one alkyl substituent increases catalytic activity in the order Me>Et>NM because electron donation tendency increases the polymerization rate whereas steric hindrance reduces it.[19]

2.4. Synthesis of Bis Cyclopentadiene Titanium Dichloride

2.4.1. Drying Procedure Of Tetrahydrofuran

THF (C_4H_8O) is a flammable and volatile organic solvent (b.p.65-67^{0}C/760 mmHg). The main impurity in THF is water which reacts in reaction medium to form undesirable products like titanium hydroxide during the formation of Biscyclopentadienyl titanium dichloride (Cp₂TiCl₂). Formation of hydroxide suppresses the production of Cp₂TiCl₂. When THF is allowed to stand for some time in contact with air and exposed to light, slight oxidation occurs with the formation of explosive peroxide. It was kept in a dark place and presence of air was avoided[20].

2.4.2. Purification of Tetrahydrofuran

One litre THF is taken in a clean.dry, single neck, two litre round bottom flask and about 1g of anhydrous calcium hydride is added. This mixture is allowed to reflux for 2 hrs and distilled. Large quantity of water is removed during this period. Next, fine sodium wire (about 10g) is introduced into the THF with the aid of a sodium press. The die is nearly filled with lumps of clean sodium, then placed in position in the press, and the plunger slowly screwed down. As soon as sodium wire emerges from the die, the flask containing THF is held immediately beneath the die, and the plunger is gradually lowered until all the sodium has been forced as a fine wire into the THF. The flask is then closed by a guard tube carrying calcium chloride to exclude moisture and escape hydrogen allowed to escape.

$$Na \quad + \quad H_2O \quad \longrightarrow \quad NaOH \quad + \quad H_2 \uparrow$$

THF is allowed to stand for 2 hours in a dark and cool place.THF is then heated under reflux in nitrogen atmosphere after adding benzophenone, until dark purple colour persists due to.formation of sodium benzophenone ketyl radical which indicates the absence of moisture in THF. Now pure THF is obtained by distilling it immediately before use.

(Benzophenone)
Colourless

Benzophenonketyl radical
(Purple in Colour)
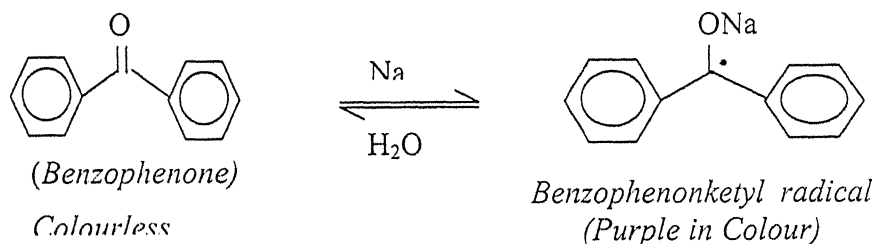
2.4.3. Preparation of cyclopentadiene (Cp) from dicyclopentadiene

Fourteen ml of dicyclopentadiene(Cp_2) is placed in the dropping funnel fitted in one litre, three-necked flask equipped with a thermometer, and a fractionating column in which chilled water is circulated at 10^0C . At the other end of the column there is a receiver which consists of a 50 ml round bottom flask immersed in a dry ice bath and protected from the air by a $CaCl_2$ dry tube.

Cp_2 Cp
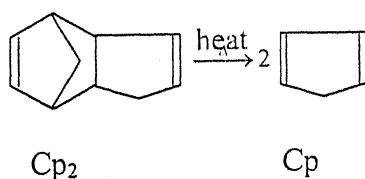
200 ml. of mineral oil is added into the flask to maintain a vapor- liquid splitting head. Now oil is heated to 240-270^0 and dicyclopentadiene is added drop wise. Cracking of Cp$_2$ to Cp takes place at this temperature The reflux ratio and the rate of addition of dicyclopentadiene is adjusted to maintain the distillation head temperature at 38- 48^{0}C, otherwise dimerization will take place and Cp is collected in 50 ml round bottom flask immersed in dry ice. Cp dimerizes rapidly at room temperature and should be used immediately or stored at dry ice temperature as obtained above and is quite satisfactory as starting material for the preparation of cyclopentadienyl anion [21].

2.4.4. Preparation of cyclopentadienyl anion

50 ml of perfectly dry xylene is added into100 ml single neck flask and small pieces of 5.74 gm sodium added into it. Xylene is refluxed till all the sodium melts then heating is stopped and xylene is removed by syringe. This molecular sodium is washed thrice with THF and transfered into a 500 ml three neck round bottem flask (RB), which has already been filled and stirred with 200 ml of THF. Cyclopentadiene is added slowly through a cannula and the solution is refluxed till an orange colour is observed[8], which is the characteristic colour of sodium salt of cyclopentadienyl anion (C$_5$H$_5$Na).

2.4.5. Preparation of Saturated Chloroform with Hydrogen Chloride

About 150ml of concentrated sulphuric acid is placed into a two neck RB and 30% (v/v) concentrated hydrochloric acid is added drop wise through a dropping funnel. Water is absorbed by sulphuric acid and hydrogen chloride gas evolved. The rate of evolution is controlled by the supply of hydrochloric acid.   This evolved gas is passed through a sulphuric acid   trap and ensuring that hydrochloric acid is perfectly dry. One can now saturate chloroform by passing hydrogen chloride gas [20].

2.4.6. Preparation of Cp$_2$TiCl$_2$

The orange solution of sodium cyclopentadienyl (C$_5$H$_5$Na) is cooled in ice a bath and THF is added with rapid stirring TiCl$_4$ is added with the help of a syringe. After stirring the reaction mixture for 3 hours, the solvent is removed under reduced pressure in a rotary evaporator.

$$2\ C_5H_5Na\ +\ TiCl_4\ \xrightarrow[0^0C]{THF}\ (C_5H_5)_2TiCl_2\ +\ 2\ NaCl$$
(as a residue)
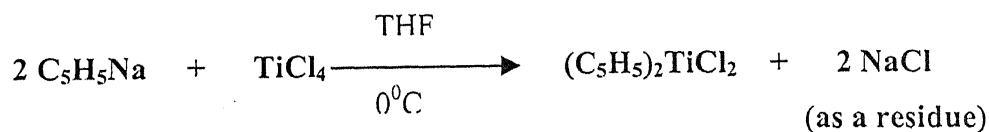
The residue was then repeatedly extracted with boiling chloroform already saturated with hydrogen chloride gas. The extract evaporated and the residue is reextracted with chloroform saturated with HCl. To cyclopentadiene titanium dichloride, chloroform is added and after saturating it with hydrogen chloride, it is cooled in a dry ice bath and saturated crystals are obtained with rapid filtration. Crystallization can occur at 70^0C in chloroform solution [21].

Table 2.1 Analysis of Cp_2TiCl_2

Compound prepared Cp_2TiCl_2	C_5H_5 Moles	Na moles	$TiCl_4$ moles	Solvent THF	Yield gm
Moles	0.2307	0.2538	0.1153	200 ml	12 gm
Molar Equivalent	1	1.1	0.5	-	-

Basis: Cp =15 gm

2.5 Characterization of Cp_2TiCl_2

2.5.1 Characterization on the basis of I.R. Spectra:

The fundamental vibrational spectra of Cp_2TiCl_2 which is synthesized in the lab (fig. A1) is similar in their major features compared with the reported IR values [22] and the value comes from commercial Cp_2TiCl_2 Fig A.1.2(Aldrich Germany) are listed below :

Table 2.2
Comparative study of I.R. spectra of Cp_2TiCl_2

Cp_2TiCl_2	S cm^{-1}	S cm^{-1}	W cm^{-1}	VW cm^{-1}	M cm^{-1}	S cm^{-1}	M cm^{-1}	VS cm^{-1}
Reported	3118	1445	1375	1131	1028	1014	868	820
Experimental	----	1442.6	1369	1130	1019	----	868	821
Commercial	3106	1442	----	----	1019	----	868	820

The high resolution of 820 cm^{-1} and a sharp splitting of 1020 cm^{-1} band are noticeable feature of the spectra of Cp2TiCl2. After comparing the IR values one can admit the purity of Cp_2TiCl_2 which has been synthesize in the lab. All five equivalent hydrogen atom positions and this equivalence is demonstrated by the very sharp over tone band at 6120 cm^{-1}. The proton magnetic resonance spectra of Cp_2TiCl_2 contain a single sharp proton line, which is sufficient to conform the above conclusion.

2.5.2 Characterization on the basis of Physical properties

Cp_2TiCl_2 is a red colour solid having melting point 289 ± 2^0C[22]. Colour of synthesized compound is same and the melting point is observed at 285^0C which slightly deviates with reported value. It can be considerd as a permissible error or impurities.

2.5.3 Characterization on the basis of ^{1}H NMR Spectra

The chemical shift in NMR proton spectra of Cp_2TiCl_2 which is synthesized in the lab (fig. A2.1) is similar to the reported values [22] and the value comes from commercial Cp_2TiCl_2 Fig A.2.2(Aldrich Germany) are listed below :

Table 2.3

Comparative study of ^{1}H NMR spectra of Cp_2TiCl_2

Cp_2TiCl_2	NMR value Chemical shift
Reported	6.58
Commercial	6.54
Experimental	6.52

It is evident from the structural formula (1) that $(\Pi\text{-}C_5H_5)_2TiCl_2$ is having only one type of proton, attached with symmetrical Π-bonded carbon atoms which gives only singlet peak in the NMR spectra. Synthesized Cp_2TiCl_2 is also showing singlet peak at 6.52, that is nearer to reported NMR values of Cp_2TiCl_2. One can say on the basis of match, among the experimental, reported, and commercial NMR values that synthesized compound is Cp_2TiCl_2.

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CHAPTER 3
SYNTHESIS and CHARACTERIZATION
OF
TRIETHYL ALUMINUM

Triethylaluminum (TEAL) is widely used as a cocatalyst in the polymerization of olefins whose involvement is crucial in the formation of active sites during the polymerization. It is also used as a starting material for the synthesis of ethyl-aluminoxane. Hence the synthesis of triethyl aluminum is important.

Triethyl aluminum is a homologue of trialkyl aluminum in which alkyl groups are attached with a central metal aluminum. Concrete examples of some other organoaluminum compounds which can replace TEAL as a cocatalyst are [1]:

a. Trialkylaluminum

Trimethylaluminum,

Triethylaluminum,

Triisopropylaluminum,

Triisobutylaluminum,

b. Alkenylaluminum halides

Dimethylaluminum chloride

Diethylaluminum chloride

Dissopropylaluminum chloride

Dissobutylaluminum chloride

3.1. Properties of tri Alkyl Aluminum:

All the trialkylaluminum compounds are colourless liquids at room temperature and generally show association property. The association phenomenon of Alkyl Aluminum has been shown by X-Ray crystallography in which alkyl groups are simultaneously bound to two or even three metal atom. In all cases, the α carbon atom of bridging alkyl groups has been found to be equidistant from both aluminum atoms and also exists as a dimer. The dimerization phenomenon has been explained [2-5] by a additional bonding between the sp^3 orbitals of the alkyl group and the vacant p orbitals of Aluminum shown in Fig. 3.1. Triethylaluminum associates in the vapour phase but less than trimethylaluminum [6,7]. The dimer of ethyl aluminum is 80% dissociated at 90^0 C, that's why purification of triethylaluminum has always been done under reduced pressure. Tri ethyl aluminum is strongly associated in liquid phase [8-10]. The dissociation of 0.01 mole fraction solution of triethylaluminum ranged from 0.4% at 0^0C, 22% at 100^0C to 90% at 200^0C[10].

Bonding   Non-Bonding   Anti-Bonding
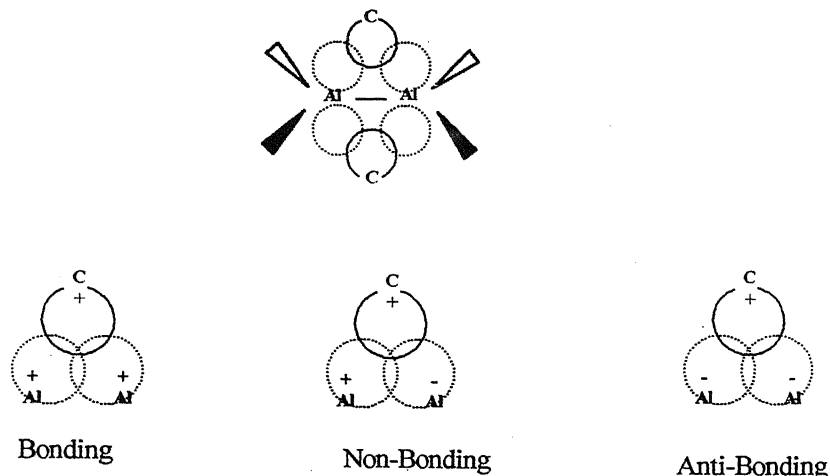
Fig.3.1: Structure and Bonding and Tri Alkyl Aluminum Dimer

The trialkyl aluminum are strong lewis acids and coordinate with electron donors to form complexes, in which the aluminum atom requires a stable octate of electrons. The complexes are usually stable enough to be purified by distillation under vacuum. The series of relative Lewis-acid strengths towards external base is in order of $R_3Al < R_2AlCl < RAlCl_2 < AlCl_3$. This is the reason why ether is always present in trialkylaluminum as a complex [11].

3.2. Synthesis for Trialkyl Aluminum [12]

3.2.1. Direct Synthesis: The direct synthesis for trialkylaluminum proceeds by Aluminum metal, hydrogen and terminal olefins.

$$2Al + 3H_2 + 6 \; \underset{R}{\overset{R}{>}}C=CH_2 \longrightarrow 2 \; (\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{CH-CH_2}})_3Al$$

{R: H , CH_3, C_2H_5)
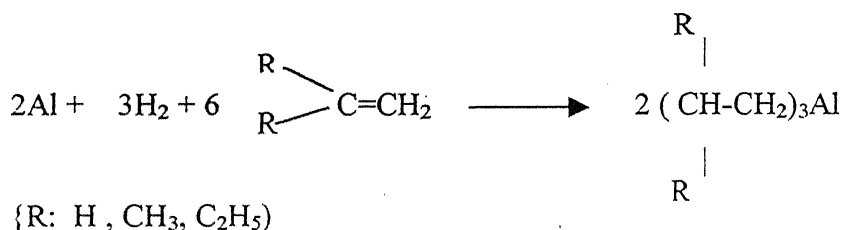
Generally triethylaluminum, tripropylaluminum and triisobutylaluminum can be synthesized by this method.

3.2.2. Synthesis From diazomethane:

When dialkylaluminum hydride reacts with diazomethane to insert a methylene group in the aluminum hydrogen bond, N_2 gas is evolved.

$$R_2Al\text{-}H + CH_2N_2 \longrightarrow R_2Al\text{-}CH_3 + N_2\uparrow$$

This reaction is more useful for the preparation of halomethyl derivatives [13-15].

3.2.3. From Grignard and organolithium reagent:

This synthesis scheme is generally used for preparation of trialkyl aluminum.When 3 moles of ethereal solution of Grignard Reagent (R-Mg-X) reacts with one mole of AlX$_3$ (Aluminum Halide) it gives the corresponding triorgano aluminum (R$_3$Al) as its etherate. Trimethylaluminum (CH$_3$)$_3$Al [16], triethylaluminum(C$_2$H$_5$)$_3$Al[17], tri-n-propylaluminum and triisopropylaluminum [18] have been prepared by this method.

$$3R\text{-}Mg\text{-}X \quad + \quad AlX_3 \quad \longrightarrow \quad R_3Al \quad + \quad \text{complex solid of Mg}$$

Optically active tris-2-methylbutylaluminum etherate has been prepared from optically active 2-methylbutyl magnesium bromide in ether. Attention is directed to the reaction of primary alkyl halide with magnesium in hydrocarbons or in complete absence of solvent[19]. The ether free organo magnesium compounds is reacted with anhydrous Aluminum Chloride to give compounds other than trimethyl aluminum [20-22]. This is particularly useful for the preparation of the higher primary alkyl aluminum compounds (R$_3$Al; R= ethyl to nonyl) [20]. Formation of the organo magnesium compound can be combined with the alkylation of aluminum chloride by treating the magnesium directly with the mixture of the alkyl halide and aluminum chloride [20 21] , but this method carries the risk of Lewis acid- catalysed elimination of hydrogen halide from alkyl halide.

3.2.4. Preparation of Grignard Reagent:
Ether free organo magnesium halide reagent is prepared by adding ether solvent slowly into boiling toluene, which is added into the anhydrous Aluminum Halide [23] to get a trialkyl solution in toluene. Toluene is removed under reduced pressure. Organo magnesium compound is redissolved in benzene before adding aluminum so as to facilitate final separation of the product by distillation [24].Triethyl aluminum has also been obtained by reaction of ethyllithium with ethylaluminum dibromide in benzene [25].

s3.3. Pyrolysis of Triethyl aluminum (TEAL)

Kinetics of the decomposition of TEAL in the vapour phase has been studied over the temperature range 162-192^{0}C. [26,27]. The volatile products were ethylene, ethane, 1-butene, cis and trans-2-Butene, hydrogen and lesser amounts of methane, butane and hexane. In the later stage of decomposition an aluminum metal and hydrogen were produced. The main process decomposes TEAL into diethyl aluminum hydride and ethylene; decomposition proceed maximum near the wall of the flask.

$$(CH_3CH_2)_3Al \xrightarrow{\hspace{3cm}} Et_2AlH \quad + \quad C_2H_4$$

Hence this is also one of the reason that triethylaluminum can never be purified at normal boiling point (228^{0}C).

3.4. Experimental Procedure For Triethylaluminum

3.4.1. Drying and Purification of Diethyl Ether (Ether)

Drying

Ether is a highly flammable and extremely volatile organic compound (b.p. 35^{0}C). The main impurity in diethyl ether is water, which reacts in reaction medium to form undesirable products like magnesium hydroxide, during the formation of Grignard Reagent; and forms aluminum hydroxide in subsequent reaction of triethylaluminum. Due to hydroxide formation, resultant product disappears; being a highly exothermic reaction it causes explosion. Furthermore, when ether is allowed to stand for some time in contact with air and exposed to light, slight oxidation occurs with the formation of the highly explosive diethyl peroxide (Et$_2$O$_3$). Ether should be kept in a dark place and the presence of air is to be avoided [28].

Purification

One litre diethyl ether is taken in a clean, dry, single neck, two litre round bottom flask and 100g of anhydrous calcium chloride is added This mixture is allowed to stand for 10 hours with occasional shaking. Large quantity of water is removed during this period. The ether is filtered through a large filter paper into another clean dry flask. Fine sodium wire (about 10g) is then introduced into the ether with the aid of a sodium press The die is nearly filled with lumps of clean sodium,then placed in position in the press, and the plunger slowly screwed down. As soon as the sodium wire emerges from the die, the

flask containing ether is held immediately beneath the die, and the plunger is gradually lowered until all the sodium has been forced as a fine wire into the ether. The flask is then closed by a guard tube carrying a calcium chloride to exclude moisture and permit escape of hydrogen.

$$Na \quad + \quad H_2O \quad \longrightarrow \quad NaOH \quad + \quad H_2 \text{ ©}$$

The ether is allowed to stand for 8 hours in a dark and cool place. The ether is then heated under reflux in nitrogen atmosphere after adding benzophenone, until the dark purple colour persists because of formation of sodium benzophenone ketyl radical, which indicates the absence of moisture in the ether. Pure ether is obtained by distilling it immediately before use.

Benzophenone
Colourless

Benzophenonketyl radical
(Purple in Colour)
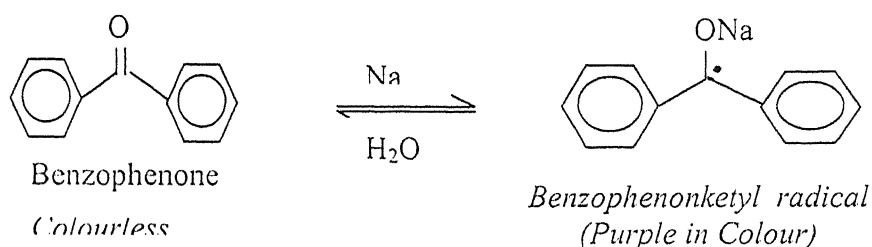
3.4.2. Preparation of Ethyl Magnesium Bromide (Grignard Reagent)

The formation of Grignard Reagent reaction is conducted in one litre three-necked round bottom flask assembly having condenser and dropping funnel. Continuous supply of dry nitrogen is provided into the flask. The condenser is used for circulation of water. Magnet is placed into the flask, which ensures agitation of the reaction mixture. Now magnesium turning is added into the flask with a pinch of iodine crystal in 200 ml Diethyl Ether solvent. The flask is placed in an ice bath to maintain 0^0C because formation of Grignard Reagent is highly exothermic; stirring the solution which turns into violet colour due to iodine crystal.Now Ethyl Bromide diluted with solvent is added dropwise with the help of dropping funnel. Immediately the violet colour disappears indicating the formation of ethyl magnesium bromide.

$$C_2H_5Br \quad + \quad Mg \text{ (Turnings)} \quad \xrightarrow[\text{Diethyl Ether}]{0^0C} \quad C_2H_5 MgBr$$
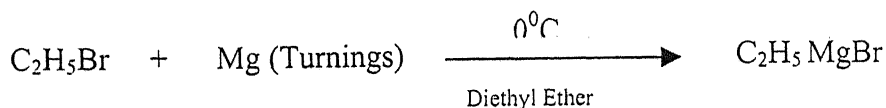
During the whole addition of ethyl bromide, temperature of reaction mixture should be maintained at 0^0C. After addition, the reaction mixture was refluxed for 2 hours at

$30\text{-}35^0C$. The Grignard Reagent is prepared with nearly 100% yield; it is highly moisture sensitive and pyrophoric . It is kept in dry N_2 atmosphere.

3.4.3. Preparation and Purification of Triethyl Aluminum

The formation of triethylaluminum with the help of Grignard reagent is conducted in one litre three necked round bottom flask assembly, having condenser and dropping funnel which supplied with dry nitrogen continuously. This reaction is highly exothermic, so it is performed at 0^0C. Putting 25 gm of anhydrous aluminum chloride in 200ml of stirred ether.

$$C_2H_5\,MgBr \quad + \quad AlCl_3 \quad \xrightarrow[\text{Ether}]{0^0C} \quad (C_2H_5)_3Al \quad + \quad \text{magnesium halide}$$
$$\textit{Triethyl aluminum} \qquad \text{\& residue}$$
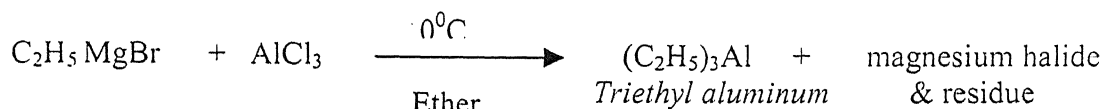
Freshly prepared Grignard Reagent is added drop wise with help of a cannula. After addition of Grignard Reagent, the mixture is refluxed for two hours by circulating the chilled water into condenser to condense the ether. After refluxing for two hours, very thick residue bed of magnesium bromide and other waste on the bottom of the flask and a yellowish brown coloured tri ethylaluminum-etherate complex solution lying over it. Purification of triethylaluminum-etherate complex is very tricky to recover Triethylaluminum.

Purification

A distillation unit is fixed into the above flask ensuring that the system should be protected by nitrogen atmosphere. Then the solution is heated at 50^0C. This ensures that all the excess ether is removed. Vacuum (25 mm Hg) is created and triethyl Aluminum is distilled out, having a trace quantity of ether, as a etherate complex at 110^0C. The trace quantity of ether which comes with triethyl Aluminum is removed by chain vacuum distillation. If the distillation of above solution carried out at its boiling point i.e. 228^0C., it is observed that the decomposition of triethyl Aluminum into gases (ethane and butane) takes place at 140^0C. To avoid the decomposition of triethyl aluminum, distillation is performed under high vacuum. When the same purification is performed with trimethyl aluminum (b.p. 130^0C), then no vacuum is required. In case of trialkyl aluminum, the rate of decomposition is directly proportional to the size of alkyl group $(CH_3 < C_2H_5 < C_3H_7)$

3.5. Characterization of Triethyl aluminum

3.5.1. On the basis of its boiling point:

Reported boiling point of triethyl aluminum is 82^0C at 4mm Hg [29] and 120^0C at 30 mm Hg [30]. In the above experiment the purification of triethyl Aluminum was observed at 110^0C / 25 mm Hg which is very near to the reported boiling point of triethyl Aluminum.

3.5.2. On the basis of physical appearance:

We know that lower molecular weight trialkyl aluminum compounds   are highly pyrophoric and hygroscopic [31]. A similar behaviour is observed when very small quantity of above prepared tri ethyl aluminum is exposed to air and moisture with the help of syringe. This physical appearance distinguishes the product as trialkyl aluminum but not specifically as tri ethyl aluminum.

3.5.3. On the basis of ^1H NMR analysis:

According to the reported data in Table 3.1 of NMR resonance [29],CH_2Al quartet peak should come in the negative side whether triethyl aluminum is complex with ether or not. Here in case of TEAL (I-V) CH_2Al quartet peak always comes in the same manner and the difference in chemical shift between triplet, because of CH_2 and quartet, CH_3 fluctuates between 1.1 to 1.21 which is almost nearer to the reported differential chemical shift that is 1.02 and increase in the separation between CH_2 (appeared at the lowest field)and the CH_3 (appeared at highest field) ring proton in the nmr spectra of the ether complex can be related to the increase in the strength of coordination of the ether molecule[29]. Hence with the help of above information one can say that TEAL (I-V) having complex with ether and also proved by δ values for CH_2 and CH_3 of TEAL(I-V) which better matches with (a) of the Table 3.1 instead of pure TEAL as in (b).

Table 3.1 Characterization of TEAL by H-NMR

Serial No.	Compound	NMR resonances (groups, δ in ppm) CH$_3$	CH$_2$Al	$\Delta\delta$ ($\delta_{CH3}-\delta_{CH2}$)
Litrature Values (TEAL)[1] [29]				
1	TEAL complex with ether	0.80, t	-0.22, q	1.02
2	TEAL (pure)	0.45, t	-0.30, q	0.75
Experimental Values (TEAL)[2]				
Run 1	TEAL 1	0.89, t	-0.22, q	1.11
Run 2	TEAL 2	1.01, t	-0.12, q	1.13
Run 3	TEAL 3	1.17, t	-0.04, q	1.21
Run 4	TEAL 4	1.17, t	-0.04, q	1.21
Run 5	TEAL5	1.17, t	-0.04, q	1.21

[1]: solvent is benzene d$_6$, [2]: solvent is CDCl$_3$, δ : Chemical shift   key: t, triplet; q, quartet;

References Chapter 3

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CHAPTER 4
SYNTHESIS and CHARACTERIZATION
OF
ETHYLALUMINOXANE

The alkylaluminoxane cocatalyst is usually formed by the controlled hydrolysis of alkyl aluminium.The structure is believed to be complex. It is consider to be either linear oligomeric or cyclic oligomeric, as illustrated in fig. 4.1

| Linear Form | Cyclic form |
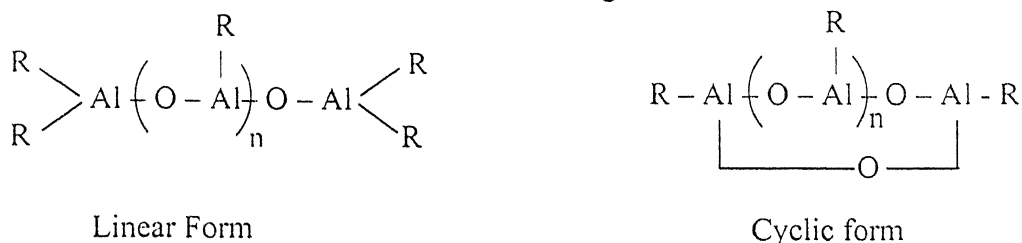
Fig. 4.1 Schematic representations of the structure of alkylaluminoxane [1,2]

The most active and therefore the most commonly used alkylaluminoxanes is methylaluminoxane (MAO) , an amorphous,pyrophoric solid that is soluble in toluene and insoluble in hexane.[3,4]The average number of aluminium units in the the cluster of (MAO) varies between 10 and 20; higher molecular weight MAO compound is insoluble.The dynamic processes of alkylaluminoxane in solution are presented in fig. 4.2 [5].
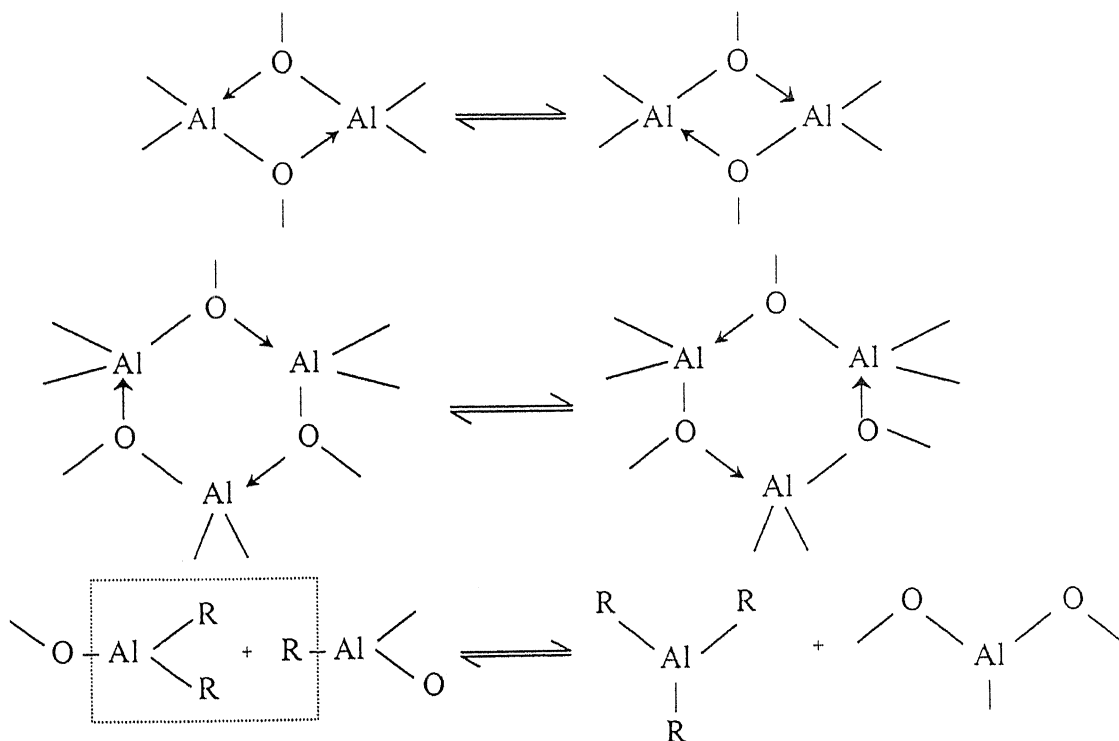
Fig. 4.2 Dynamic processes of Alkylaluminoxane in solution

The catalyst activity is strongly influenced by n, the degree of oligomerization, and the most effective range of Aluminoxane is $3 < n < 50$ depending on the metallocene type and co composition with TEAL. Cp_2ZrMe_2 has its highest activity when n is greater than 10, but for CP_2ZrCl_2 and Ind_2ZrCl_2, activity is reported to vary between n, values of 3 and 50. The concentration of aluminoxane in the catalyst system affects the polyolefin properties. To produce a higher molecular weight polymer, the optimum ratio of polymer in the alkyl aluminium to the total metal in the metallocene depends on the metallocene type and the experimental condition. Extensive investigations have shown that the ratio could range between 50-100 for supported and 400 – 20,000 for unsupported catalyst system [6].

4.1 CHEMISTRY OF ALUMINOXANE

Aluminoxanes have been extensively studied because of their catalytic properties. Aluminoxanes are usually obtained by the following reaction [1,2] (eq.1)

$$2n \; R_3Al + nH_2O \; \rightarrow \; (R_2Al\text{-}O\text{-}AlR_2)n + 2n \; RH \uparrow \qquad (1)$$
$$\mathbf{I}$$
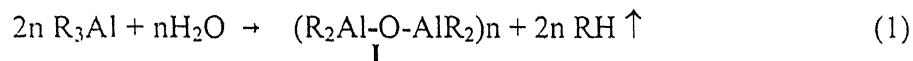
In the case of R=Et, it is assumed that the product **I** is trimeric [7]. The work is motivated by the observation that during purification of aluminoxane in vacuum at room temperature. It is possible to distill off nearly one mole of R_3Al from I to yield a highly viscous oligomeric residue. The procedure is reversible even at elevated temperature, i.e. the residue dissolved in the removed R_3Al to re-form I.

A preliminary account has appeared in [5]

4.1.1 Reaction of Et_3Al with H_2O at 1/1 molar ratio

The reaction between equimolar amounts of Et_3Al and H_2O is carried out in diethyl ether or toluene in the temperature range -70^0C to room temperature. With diethyl ether as a solvent, the product mixture is slightly opalescent homogeneous solution, but after several days a precipitate is observed. During the reaction in toluene, precipitation starts coming before the reaction ended.

It is important to note that during the reaction less than 2 mol of ethane per 1 mol of H_2O is evolved [4]. The product II is, isolated by distilling off the solvent under reduced pressure at room temperature (eq.2).

$$n \; Et_3Al + nH_2O \xrightarrow[\substack{Et_2O \, or \, PhCH_3}]{-70 \, to \, 20^0 \, C} \; Et_2Al(OAlEt)_{n-1}OH + (2n-1)EtH \uparrow \qquad (2)$$
$$\textbf{II}$$
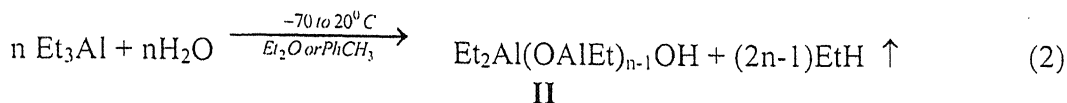
It is a white amorphous powder, insoluble in organic solvents for higher value of n. The amorphous structure of II is confirmed by X-ray examination. The Al content of II varies in the range 33.5-34.5% Al, suggesting a non-selective course of reaction and incomplete reaction of OH groups. Had all OH groups reacted, the product II might have a cyclic or very long chain structure, and the Al content has been 37.5%. Thus the product II seems to be a mixture of oligomers, i.e. several fractions differing in the number of OAlEt units, formed by uncontrolled oligomerization in reaction (2). For simplicity, equations are written only for one fraction with a fixed but unspecified value of n.Use of slight excess of Et_3Al in the reaction leads to the same amorphous powder, insoluble in organic solvents, 2 mol of EtH is evolved (eq.3).

$$(n + 1) \; Et_3Al + nH_2O \xrightarrow[\substack{Et_2O \, or \, PhCH_3}]{-70 \, to \, 20^0 \, C} \; Et_2Al(OAlEt)_{n-1}OAlEt_2 + 2n \; EtH \uparrow \qquad (3)$$
$$\textbf{III}$$
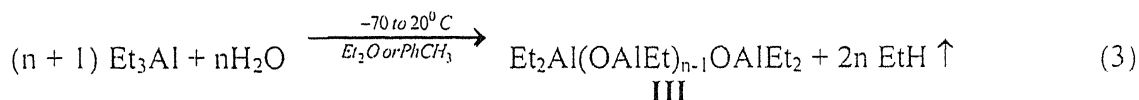
Product II dissolves in organometallic compounds (Et_3Al, Me_3Al, $EtAlCl_2$, Et_2Zn etc.) with evolution of small amounts of the relevant hydrocarbon. To solubilize II at least an equimolar quantity of metalloorganic compound is required (eq.4).

$$Et_2Al(OAlEt)_{n-1}OH + n \; R_3Al \xrightarrow[\substack{no \, solvent}]{20^0 \, C} [Et_2Al(OAlEt)_{n-1}OAlR_2 \, (n-1)R_3Al] + RH \uparrow \quad (4)$$
$$\textbf{II} \qquad\qquad\qquad\qquad\qquad \textbf{IV}$$
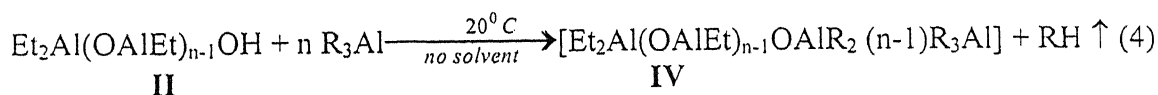
It is clear from the reactions 2,3 and 4, that a 1/n-th part of the R_3Al taken is used in the reaction with OH groups of product II, and the remaining (n-1)/n-th part dissolves the product III to give IV.

4.1.2. Alternative synthesis of tetraethylaluminoxane

The addition of the second mol of Et_3Al to the product II yields an oily, colourless, slightly opalescent liquid soluble in organic solvents (eq.5)

$$\text{Et}_2\text{Al(OAlEt)}_{n-1}\text{OH} + n\ \text{R}_3\text{Al} \xrightarrow[\textit{no solvent}]{20^0 C} \text{EtH} + [\text{Et}_2\text{Al(OAlEt)}_{n-1}\text{OAlEt}_2\ (\text{n-1})\text{Et}_3\text{Al}]\ (5)$$

$$\textbf{II} \hspace{8cm} \textbf{V}$$
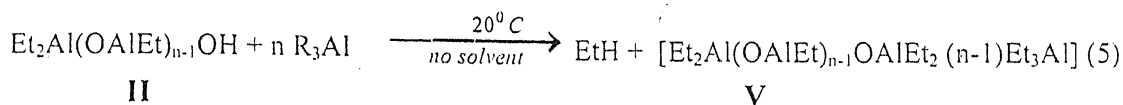
It should be noted that reaction 2 and 5 are stoichiometrically equivalent to reaction 1.

The identification of V is based on ^{1}H NMR and IR spectra, elemental analysis, and behaviour in vacuum at room and elevated temperature. The product V is found to be exactly equivalent to the tetraethylaluminoxane obtained in reaction (1), i.e. to the tetraethylaluminoxane I [3]. It is also found that in vacuum at elevated temperature product I yielded III, and the process is reversible:

$$(\text{Et}_2\text{Al-O-AlEt}_2)\text{n} \rightleftharpoons (\text{n-1})\text{Et}_3\text{Al} +\ \text{Et}_2\text{Al(OAlEt)}_{n-1}\text{OAlEt}_2$$

$$\textbf{I} \hspace{7cm} \textbf{III}$$
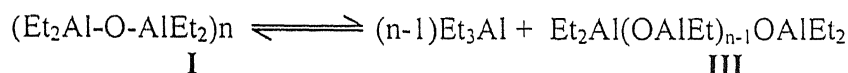
4.1.3. Complexation of ethylaluminoxanes by strong Lewis acids:

Reaction of II with equimolar quantity of Me$_3$Al yields an oily, opalescent, colourles liquid, soluble in organic solvents (eq.6).

$$\text{Et}_2\text{Al(OAlEt)}_{n-1}\text{OH} + n\ \text{Me}_3\text{Al} \xrightarrow[\textit{no solvent}]{20^0 C} \text{MeH} + [\text{Et}_2\text{Al(OAlEt)}_{n-1}\text{OAlMe}_2\ (\text{n-1})\text{Me}_3\text{Al}]\ (6)$$

$$\textbf{II} \hspace{8cm} \textbf{VI}$$
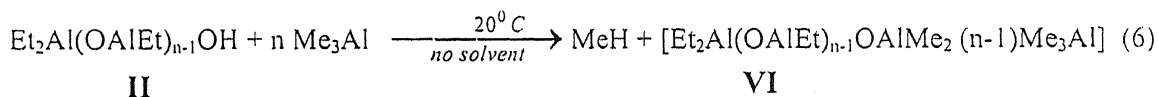
The dissolution is exothermic, and small amounts of methane are evolved. Signals from Me$_3$Al protons is found in ^{1}H NMR spectrum of the product VI, as well as two markedly broadened signals from the ethyl groups in the oligomeric portion. Distillation gives only Me$_3$Al, and there has been no exchange of Et and Me groups. The products II and III dissolved in BF$_3$.OMe$_2$; the temperature increased significantly on dissolution, and rapid evolution of gaseous dimethyl ether is observed, and at the same time BF$_3$ complexed with the oligomer:

$$\text{Et}_2\text{Al(OAlEt)}_{n-1}\text{OAlEt}_2 + (\text{n-1})\text{BF}_3.\text{OMe}_2 \xrightarrow[\textit{no solvent}]{20^0 C} \text{Me}_2\text{O}\uparrow + [\text{Et}_2\text{Al(OAlEt)}_{n-1}\text{OAlEt}_2.(\text{n-1})\text{BF}_3]\ (7)$$

$$\textbf{III} \hspace{8cm} \textbf{VII}$$
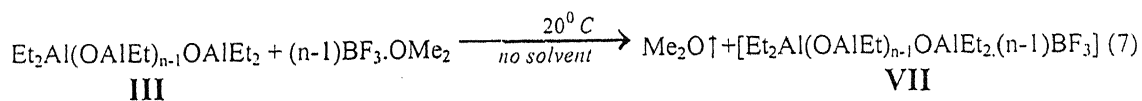
The complex VII is unstable at room temperature, and decomposes with slow evolution of BF$_3$.After several hours product III is recovered (eq. 8).

$$[Et_2Al(OAlEt)_{n-1}OAlEt_2.(n-1)BF_3] \xrightarrow{\ Room\ temp.\ } (n-1)BF_3 \uparrow + Et_2Al(OAlEt)_{n-1}OAlEt_2. \quad (8)$$

$$\textbf{VII} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{III}$$
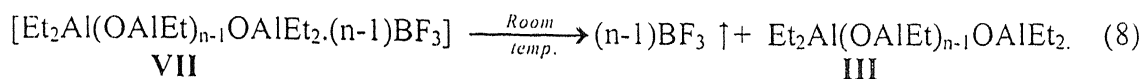
Aluminoxanes can be considered as a special case of equilibrium complexes of the strong Lewis acid (R_3Al) with an oligomeric species (eq.9).

$$R_2Al(OAlR)_{n-1}OAlR_2.(n-1)\,R_3Al \rightleftharpoons R_2Al(OAlR)_{n-1}OAlR_2 + \frac{n-1}{2}(R_3Al)_2 \quad (9)$$
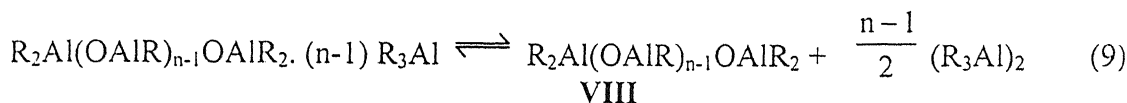
$$\textbf{VIII}$$

There is a dynamic equilibrium VIII with tetraethylaluminoxane, $(R = Et)$, because of the comparable Lewis acidities of Et_3Al and acidic sites in the oligomer, with the result that there is a competition between equilibrium and I complex of oligomers and Et_3Al and II two oligomeric chain clusters.

It is now clear that when reaction of equimolar amounts of Et_3Al and H_2O, (eq. 2) is carried out in a polar solvent like diethylether (Et_2O), precipitation of the oligomer II is inhibited because of the competition between the polar solvent and oligomeric clusters, while in nonpolar solvent (toluene) the precipitation occurs readily.

The properties of tetraethylaluminoxane and its complexes with electron donors can be better explained in terms of the proposed structure by assuming that tetraethylaluminoxane is normally trimeric [3], which is complexed with electron donors in the presence of oligomeric carrier [8].
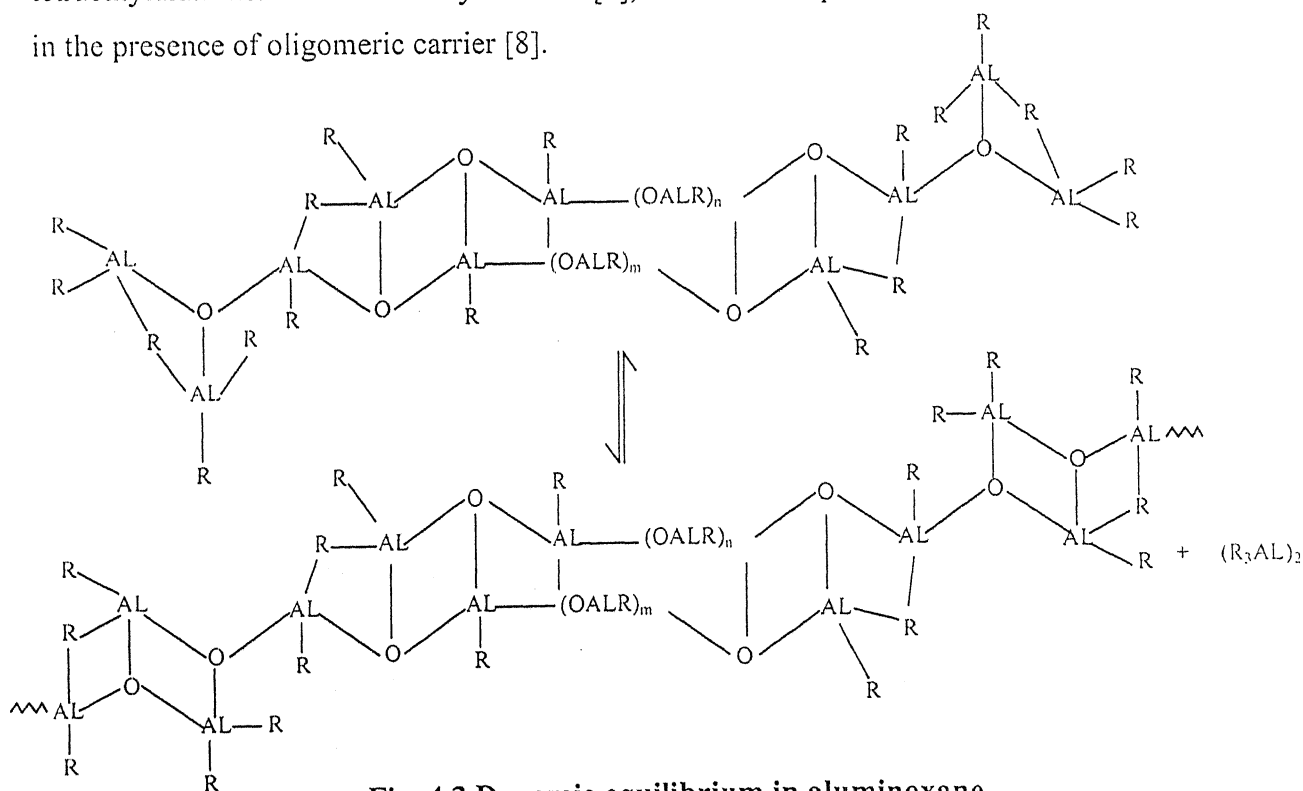
Fig. 4.3 Dynamic equilibrium in aluminoxane

4.2 Reported procedures for Ethylaluminoxane

4.2.1. Ethylaluminoxane via $CuSO_4.5H_2O$:

A 2 liter round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, and a dropping funnel is placed pulverized $CuSO_4.5H_2O$ and add 200 mL of toluene. Toluene solution of $Al(C_2H_5)_3$ is added drop wise at -20^0C. After 24 hrs. the reaction temperature is slowly raised to 20^0C. After filtration, a clear toluene solution is obtained and solution is concentrated under reduced pressure. A glossy residue is obtained which is added in 1 : 1 toluene/n-hexane mixture. This process is repeated several times to ensure complete removal of distillable $Al(C_2H_5)_3$. On drying at 40^0C and 1×10^{-6} mm Hg, a white, apparently crystalline solid is obtained [9].

4.2.2. Ethylaluminoxane via $Al_2(SO_4)_3.14H_2O$.

A 400 ml flask thoroughly purged with nitrogen is charged with $Al_2(SO_4)_3.14H_2O$ and 125 ml of toluene. The contents are cooled to 0^0C, and triethylaluminum diluted with 125 ml of toluene is added dropwise. The resultant mixture is warmed to 40^0C, and the reaction is continued at the temperature for 24 hours. After the completion of the reaction, the reaction mixture is subjected to solid-liquid separation by filtering, and toluene is removed from the filtrate, whereby white solid is obtained [10].

4.2.3. Ethylaluminoxane via pure water:

In toluene solution of $Al(C_2H_5)_3$, a solution of H_2O in 800 mL of $(C_2H_5)_2O$ is added dropwise at -78^0C. The mixture is stirred and warmed slowly to room temperature. Stirring is maintained for 24 hrs until gas evolution observed. The solvent is distilled off under reduced pressure and toluene is added to the residue. The procedure is repeated several times to give a white amorphous power [9].

4.3 Experimental Procedure For Ethylaluminoxane

Synthesis of ethylaluminoxane is done by two different methods. In first method $Al_2(SO_4)_3.14H_2O$ is used as a water source for the toluene solution of tri ethylaluminium but in second method the requirement is fulfil by using pure water. Toluene is used as solvent in both syntheses.

4.3.1. Drying of Toluene

One litre toluene is taken in a clean, dry, single neck, two litre round bottom flask and 100g of anhydrous calcium chloride is added This mixture is allowed to stand for 10 hours with occasional shaking. Large quantity of water is removed during this period. The toluene is filtered through a large filter paper into another clean dry flask. Fine sodium wire (about 10g) is then introduced into the ether with the aid of a sodium press The die is nearly filled with lumps of clean sodium, then placed in position in the press, and the plunger slowly screwed down. As soon as the sodium wire emerges from the die, the flask containing ether is held immediately beneath the die, and the plunger is gradually lowered until all the sodium has been forced as a fine wire into the ether. The flask is then closed by a guard tube carrying a calcium chloride to exclude moisture and permit escape of hydrogen.

$$Na \quad + \quad H_2O \quad \longrightarrow \quad NaOH \quad + \quad H_2 \text{ ©}$$

The toluene is allowed to stand for 8 hours in a dark and cool place. The is then toluene heated under reflux in nitrogen atmosphere after adding benzophenone, until the dark purple colour persists because of formation of sodium benzophenone ketyl radical, which indicates the absence of moisture in the ether. Pure toluene is obtained by distilling it immediately before use.

4.3.2 Experimental Procedure For Ethylaluminoxane using $Al_2(SO_4)_3.14H_2O$

One liter flask thoroughly purged with nitrogen is charged with 16.7gm $Al_2(SO_4)_3.14H_2O$ and 200ml of toluene is added into it. The contents is cooled to -20^0C, and 29 ml of triethylaluminum is diluted with 500 ml of toluene and added dropwise. After addition the resultant mixture is warmed to 40^0C, and the reaction is continued at the temperature for 24 hours. After the completion of the reaction, the reaction mixture is subjected to solid-liquid separation by filtering, and toluene is removed from the filtrate, whereby 200mg white solid is obtained

4.3.3 Experimental Procedure For Ethylaluminoxane using Pure Water

Two liter flask thoroughly purged with nitrogen is charged with 26ml of TEAL in 200ml of perfectly dry toluene and 3.422ml H_2O in 800 mL of $(C_2H_5)_2O$ is added dropwise at -78^0C. The mixture is stirred and warmed slowly to room temperature. Stirring is maintained for 24 hrs until gas evolution observed. The solvent is distilled off under reduced pressure and toluene is added to the residue. The procedure is repeated several times to give a white amorphous power calling as EAO-II [9].

4.4 Characterization of Ethylaluminoxane

Characterization is done for both EAO-I and EAO-II

4.4.1 On the basis of physical appearance:

According to the literature ethyl aluminoxane is a white amorphous powder. And product (EAO), which synthesized is same.

4.4.2 On the basis of FTIR spectrum:

According to the reported FTIR spectrum of ethyl aluminoxane ($Et_2AlOAlEt_2$) appears to be composed of $AlEt_3$ plus some broad absorption around 790 –815 cm^{-1}. IR spectrum showed absorption band at 802 cm^{-1} characteristic of Al-O-Al linkage. IR spectrum of the ethoxy derivetives having chracteristic bands are assigned to C-O stretching viberations in the region 1020-1110 cm^{-1} [11]. It indicate that the ether is present which comes with starting material(Et_3Al)

Table: FTIR data of ethylaluminoxane.

ETHYLALUMINOXANE	$V_{CH3(asy)}$ (cm^{-1})	$V_{CH3(sym)}$ cm^{-1}	V_{C-Ot} cm^{-1}	$V_{Al-O-Al}$ cm^{-1}	V_{Al-CH2} cm^{-1}
Reported	1452, m	1380	1072-1110	790-815	654
Experimental	1456, m	1381	1099	802	657

On the basis of FTIR spectrum of compound one can say ethyl aluminoxane is prepared with some ethoxy group compounds. It is not perfectly pure.

4.4.3 On the basis of XRD Data

X ray differection pattern demonstrated the absence of crystallinity in the material (EAO-I and EAO-II).

Hence (EAO-I and EAO-II) are amorphus in nature, which are matches with reported behavior.

Distillation of EAO is very difficult because its boiling point is 45-51 ^{0}C at 8 x 10 $^{-4}$ mm Hg.

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CHAPTER 5

POLYMERIZATION OF ETHYLENE

5.1 Experimental Details for Polymerization of Ethylene

All the experiments for polymerization of ethylene has been done in two litre batch reactor. Various polymerization run is performed in perfectly dry n-Hexane solvent for four different type of catalyst combinations which are $TiCl_4$/TEAL, $ZrCl_4$/TEAL, unsupported Cp_2TiCl_2/TEAL/EAO-II and SiO_2 supported Cp_2TiCl_2/TEAL/EAO-I. Hydrogen is use as a chain-terminating agent for all the polymerization run.

Experimental setup in which polymerization is performed shown in Fig. 5.1

A = Two litre batch reactor

B = Heating coil

T/C = Temperature Indication and Controller

D = Cooling water circulating coil
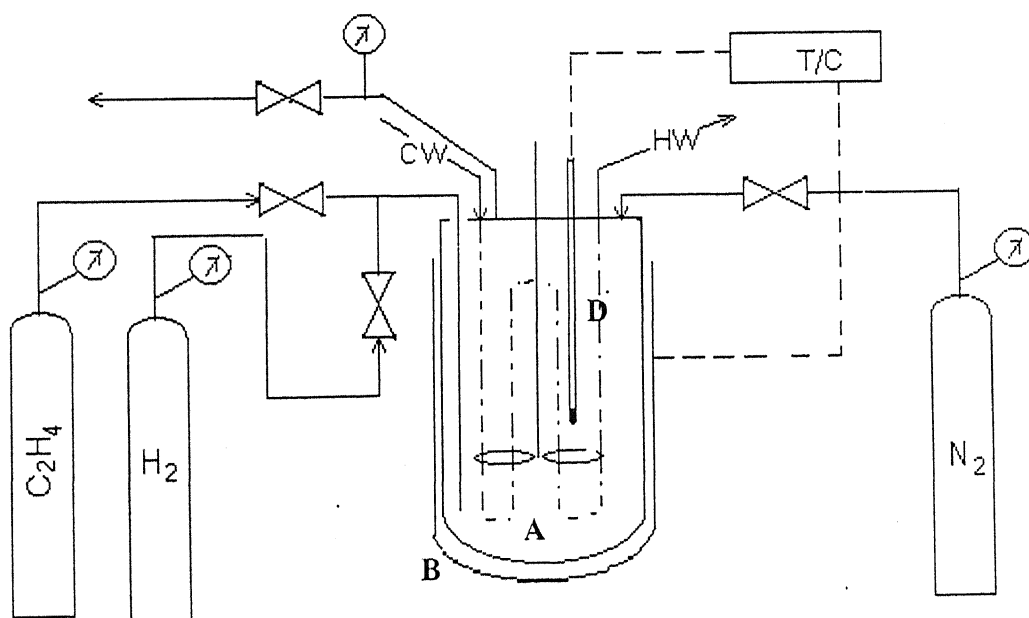
Fig.5.1 Experimental Setup For Polymerization of Ethylene

5.2 Polymerization of Ethylene using $TiCl_4$ / Et_3Al Catalyst

One litre of dry n-hexane is introduced into two litre stainless steel reactor fully purged N_2, and the temperature raised to 40^0C. Then calculated amount of both $TiCl_4$ and TEAL is charged into the reactor and the temperature raised to 70^0 C. Subsequently, ethylene is introduced and the total pressure set at 6 kg/ cm^2 (g). This polymerization is continued for one hour while maintaining the total pressure 6 kg/cm^2 (g). After Polymerization, polymer slurry is separated by filtration and dried at 80^0C to get a fibrous polymer. Similarly, five different experiment is performed using Al / Ti molar ratio which are 5,20,50,100 and 200 mentioned below [1] .

Table – 5.1
Polymerization Run for Polyethylene
using $TiCl_4$ / Et_3Al Catalyst at 6 atm,, for 1h in n-Haxane, 70^0C

Run No.	Et_3Al (mole)	$TiCl_4$ (mmole)	Al/Ti	H_2 atm (initial)	Polymer Yield in gms	Activity (gPE/molTi) h[-1] x10[-4]	Polymer
1	0.016	3.2	5	1	75	2.34	PV III
2.	0.016	0.8	20	1	53.3	6.66	PV-IX
3.	0.016	0.32	50	1	34.77	10.8	PV-X
4.	0.016	0.16	100	1	7.9	4.94	PV-XI
5.	0.016	0.08	200	1	12.33	15.41	PV-XII

5.3 Polymerization of Ethylene using $ZrCl_4$ / Et_3Al Catalyst

One litre of dry n-hexane is introduced into two litre stainless steel reactor fully purged N_2, and the temperature raised to 40^0C. Then calculated amount of both $ZrCl_4$ and TEAL is charged into the reactor and the temperature raised to 70^0 C. Subsequently, ethylene is introduced and the total pressure set at 6 kg/ cm^2 (g) [2]. This polymerization is continued for one hour while maintaining the total pressure 6 kg/cm^2 (g). After Polymerization, polymer slurry is separated by filtration and dried at 80^0C to get a fibrous, film type polymer. Similarly, two different experiment is performed using Al / Zr molar ratio which are 5 and 10 mentioned below .

Table – 5.2
Polymerization Run for Polyethylene
using $ZrCl_4$ / Et_3Al Catalyst at 6 atm., for 1h in n-Hexane, 70^0C

Run No.	Et_3Al (Mole)	$ZrCl_4$ (mmole)	Al/Zr	H_2 atm (Initial)	Polymer Yield in gms	Activity (gPE/mole Zr) h^{-1} $X10^{-4}$	Polymer
1	0.016	3.2	5	1	3.6	0.1125	PV-VI
2	0.016	1.5	10	1	3	0.2000	PV-XIII

5.4 Polymerization of Ethylene using Unsupported Cp_2TiCl_2/EAO/TEAL catalyst:

One litre of dry n-hexane is introduced into two litre stainless steel reactor fully purged N_2, and the temperature raised to 40^0C. Then calculated amount of Cp_2TiCl_2 (100 mg) /EAO(1 gm) /TEAL (8.28 ml) having molar ratio (Al/Ti = 1250) is charged into the reasctor and the temperature raised to 70^0 C. Subsequently, ethylene is introduced and total pressure set at 6 kg/ cm^2 (g). This polymerization is continued for one hour while maintaining the total pressure 6 kg/cm^2 (g). After Polymerization, polymer slurry is separated by filtration and dried at 80^0C to get 12 gm of non fibrous powdered polymer (PV XV) [2].

5.5 Preparation of SiO$_2$ Supported (Cp$_2$TiCl$_2$/EAO/TEAL) Catalyst

A 100ml flask thoroughly purged with N$_2$ gas, charged with 0.135 gm of SiO$_2$ (from Aldrich; Germany) and 5 ml of perfectly dry toluene to form a suspension. Then 2 ml of 0.4 M triethyl aluminium in toluene is added into it and the mixture is stirred at room temperature for 30 min. successively. Then 10 ml solution of 0.194 gm Ethylaluminium (EAO) is added and the reaction mixture stirred at room temperature for 30 min. Furthermore 20 ml of toluene solution of 0.0018 gm Cp$_2$TiCl$_2$ is added and the resultant mixture was stirred for 10hr. Now solvent is removed by evaporation under N$_2$ atmosphere to get solid supported catalyst [3].

5.6 Polymerization of Ethylene using Supported Cp$_2$TiCl$_2$/EAO/TEAL Catalyst:

110gm of NaCl is added into reactor and connected with vacuum, maintaining temp. up to 90^{0}C for 30 min. Again reactor is purged with N$_2$ and 1 litre of dry n-Hexane is added into the reactor. Then supported catalyst is added & stirred for 15 minutes. Then (C$_2$H$_5$)$_3$ Al is added & stirred for 10min. & raise temp. up to 70^{0}C. Now Ethylene gas is introduced into the reactor successfully and polymerization reaction is started with the total pressure 7kg /cm^2 (g) .The polymerization is carried out at 70^{0}C for one hour. As soon as the reactor is opened, no polymer is found .It shows that polymerization is completely failed. It shows that either the supported catalyst was inactive or the system had absorbed the moisture [3].

Reason for Failure:

1. During the experiment, ethylene or nitrogen may not be purified in terms of oxygen and moisture, which is poisonous for the catalyst. Hence it must be ensured to remove the trace of residual oxygen and moisture by using column packed with oxygen scavenger and molecular sieve.

2. n- Hexane used in polymerization and toluene in preparation of supported catalyst may not be perfectly dry.

3. During the preparation of Silica supported catalyst, role of SiO$_2$ is very critical because there are many types of surface groups lie on the silica surface : (a)single hydroxyl (3740-3750 cm^{-1})which is responsible to interlink the bond between silica and cocatalyst (EAO , TEAL) (b) hydrogen bond hydroxyl group (3650 cm^{-1}), (c) paired

hydroxyl (3740 – 3750 cm^{-1})and (d) absorbed water (3265- 3645 cm^{-1}). After dehydration at 600^{0}C under nitrogen atmosphere, only single hydroxyl group remained and disappears during the reaction with ethyl aluminoxane or tri ethyl aluminum. SiO$_2$ support used in this experiment shows IR 3496 cm^{-1} which lie somewhere in the region of absorbed water on the silica surface. It may also be one reason that the catalyst was inactive during the preparation [4]

| 3740-3750 cm^{-1} | 3650 cm^{-1} | 3740-3750 cm^{-1} | 3265-3645 cm^{-1} |

Dehydration at 600^{0}C for 10 hrs.

Si-OH + EAO $\longrightarrow$ Si-O-EAO (A) + C$_2$H$_6$

Si-OH + Et$_3$Al $\longrightarrow$ Si-O-Et$_3$Al (B) + C$_2$H$_6$

Cp$_2$TiCl$_2$

A-CpTi$^+$Cl
B-CpTi$^+$Cl
Ethylmetallocenium ion
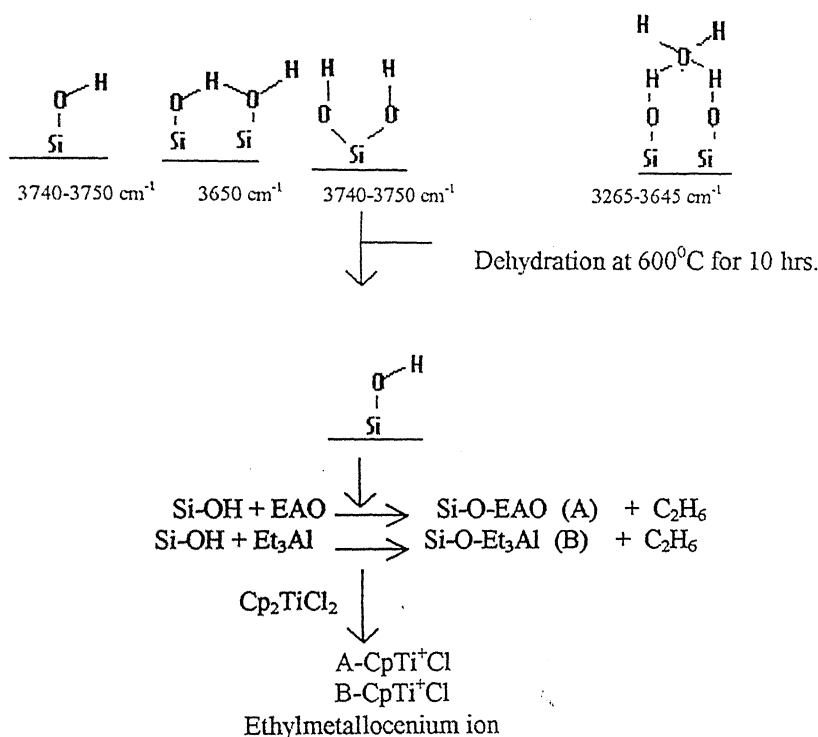
Fig. 5.2 Model of Active Site for different SiO$_2$ supported Cp$_2$TiCl$_2$[5]

5.7 Characterization of Polyethylene:

Polymerization of ethylene is performed by taking four combination of catalysts which are TiCl$_4$/TEAL , ZrCl$_4$/TEAL , Cp$_2$TiCl$_2$/TEAL/EAO and SiO$_2$ supported catalysts. Result of SiO$_2$ supported catalysts is negative.

Polymerization of ethylene is successfully proceeded by using TiCl$_4$/TEAL catalysts to form polyethylene like PV-III, PV IX ,PV-X, PV-XI and PV XII which are formed after taking Al/Ti molar ratio 5:20 50,100 and 200.All the polymer samples are fibrous in nature.

5.7.1. On the basis of FTIR Spectra

IR spectra of all polymer samples is similar to the reported IR spectra of polyethylene listed in the appendix A1 and the peaks are tabulated below in table 5.3.The structure of the repeat unit (CH_2-CH_2)$_n$ has been identified from the IR spectra at 720 cm^{-1}[7]. This is the characteristic peak for polyethylene. The peak at 1485-1445 cm^{-1} is assigned to (C-C) streching which is similar to the experimental (C-C) streching lies 1467± 1 for all the samples of polyethylene .In the same way, C-H (symmetric and asymmetric) streching band for CH_2 lies in the region of 2863-2843 cm^{-1} and 2936-2916 cm^{-1} respectively which matches with experimental as well as samples provided by GAIL. One more peak lies in the region between 37292-3782 is shown by the experimental samples and the sample provided by GAIL which is 3753 cm^{-1}, which are also similar for ZrCAl$_4$/TEAL and Cp$_2$TiCl$_2$/TEAL/EAO.

Table 5.3 Reported & Experimental FTIR Spectra of Polyethylene

POLYETHYLENE	Skeletan -(CH$_2$)$_n$-band (cm^{-1}	C-H deformation band(cm^{-1})	C-H stretching band(cm^{-1}) Sym.	C-H stretching band(cm^{-1}) Asym.	-
Reported values[6]	720	1463	2848	2920	-
GAIL values	720	1467	2848	2920	3753
Experimental Values					
PV- III	721	1466	2850	2919	-
PV-IV	720	1466	2848	2920	-
PV-VI	719	1467	2848	2918	-
PV-IX	720	1467	2849	2918	-
PV-X	721	1468	2849	2917	3782
PV-XI	720	1467	2848	2917	3729
PV-XII	720	1466	2849	2921	3741
PV-XIII	721	1468	2850	2920	3775
PV-XV	721	1467	2849	2919	3741

5.7.2 On the basis of Thermal Analysis

The thermal analysis* is carried out by Perkin –Elmer differential scanning calorie meter unit on 5.4 mg sample for PV-III and PV-IV. In this study the temperature for endothermic peak is defined as the melting point of polymer which are 133.712^{0}C and 137.72^{0}C for PV-III and PV-IV .As we know that melting point of HDPE[8] is around 140^{0}C and for LDP it is 135^{0}C.Melting point of PV-III comes nearer to LDPE but for PV-IV is shifted towards HDPE region.Melting endotherm of both samples are smooth, sharp and somewhat broader peaks[9].

* results are attached on page 116 &117

Heat of fusion(ΔH_f) is calculated for both samples (PV-III and PV-IV) i.e. 203.78 joule/gm and 189.67 joule/gm respectively. As for ΔH_F, it decreases with inctrease in melting point and molecular weight becomes larger when ΔH_f decreases[10].

It s formed from the above fact that density of polymer increases with increase in melting point and shifted towards HDPE region.This indicates that higher molecular weight affects crystallinity through chain entanglements and partially remains in amorphous state.

5.7.3 On the Basis of C and H % Analysis

one calculates C and H% for polyethylene it comes around 86% and 13.5%.But in case of lab samples, only PV-IX shows C, H% values nearer to the sample provided by GAIL i.e. 82.6% for carbon and 13.13 for hydrogen. Polymer sample (PV-XIV) prepared by using Cp_2TiCl_2/TEAL/EAO shows lower carbon and hydrogen values i.e. 61.61 and 10.92% .Reason for low carbon , hydrogen values may be because of impurities in catalyst and aluminum hydroxide etc. generated by catalyst.

<p align="center">Table 5.4 Commercial & Experimental C, H (%) Analysis</p>

POLYETHYLENE	% Carbon	% Hydrogen
GAIL values	84.56	13.55
Experimental Values		
PV-IV	77.12	12
PV-VI	69.58	10.79
PV-IX	82.61	13.13
PV-X	80.88	13.21
PV-XI	79.02	12.7994
PV-XII	80.84	13.11
PV-XIII	72.72	12.05
PV-XV	61.61	10.92

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Chapter 6

Results and Discussion

Productivity of Polyethylene using TiCl$_4$/ TEAL as a Catalyst

The activity of a Ziegler-Natta Catalyst is usually given either in gm polymer / gm titanium h^{-1} or gm polymer / gm mole Ti h^{-1} .These units are adequate for comparing catalyst, based on the same transition metal at the same temperature. The effect of [TiCl$_4$] and [TEAL] were investigated by holding the [TEAL] constant while varying the concentration of [TiCl$_4$]. The productivity of Polyethylene at TiCl$_4$ = 3.2, 0.8, 0.32, 0.16 and 0.08 m moles in the ratio of 5: 20: 50: 100: 200 are 2.34 x 10^4, 6.66 x 10^4, 1.08 x 10^5, 4.94x10^4 and 1.541x 10^5 respectively. Both the shape of the polymerization rate profile and the productivity are largely increases with the decrease of TiCl$_4$ shown in fig.6.1. It shows the activity is largely increases up to Al/Ti=50 and then slope reduces which indicates that activity is somewhere independent with Al/Ti ratio. Unexpected result arises at Al/Ti=100 because of very low activity, this can be possible due to moisture present in the solvent which is highly responsible for deactivation of catalyst.
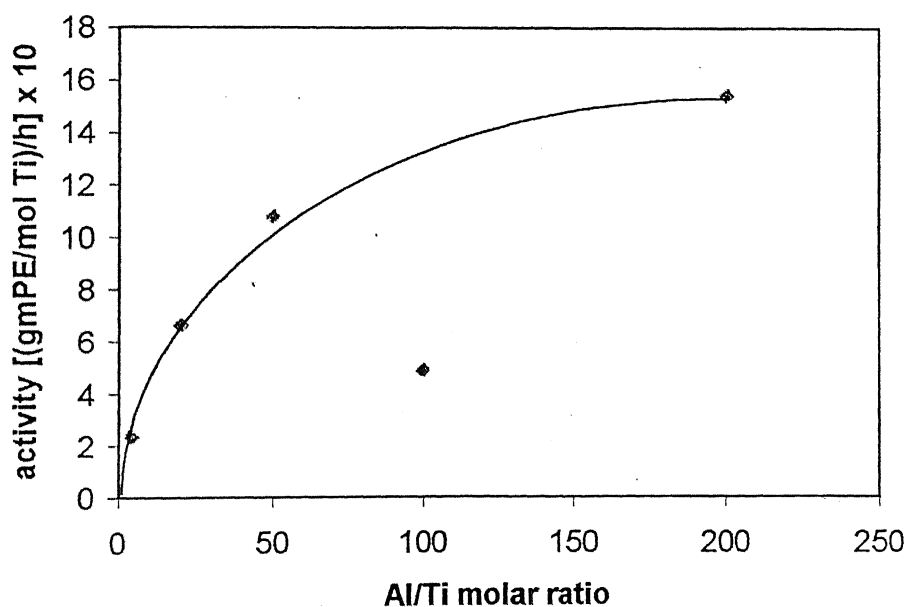
Fig. 6.1 Activity vs Al/Ti (molar ratio) for TiCl$_4$ / [TEAL] catalyst

Productivity of Polyethylene using ZrCl₄/ TEAL as a Catalyst

The effect of [ZrCl$_4$] and [TEAL] were investigated by holding the [TEAL] constant while varying the concentration of [ZrCl$_4$]. The productivity of Polyethylene at ZrCl$_4$ = 3.2and 1.5 m moles in the ratio of 5: 10 are 0.1125x $10^4$and 0.2 x 10^4 respectively. The shape of the polymerization rate profile are more or less parrellel to x axis hence the productivity are nearly constant with the decrease ZrCl$_4$ shown in fig.6.2 and very low in comperision of TiCl$_4$/ TEAL .
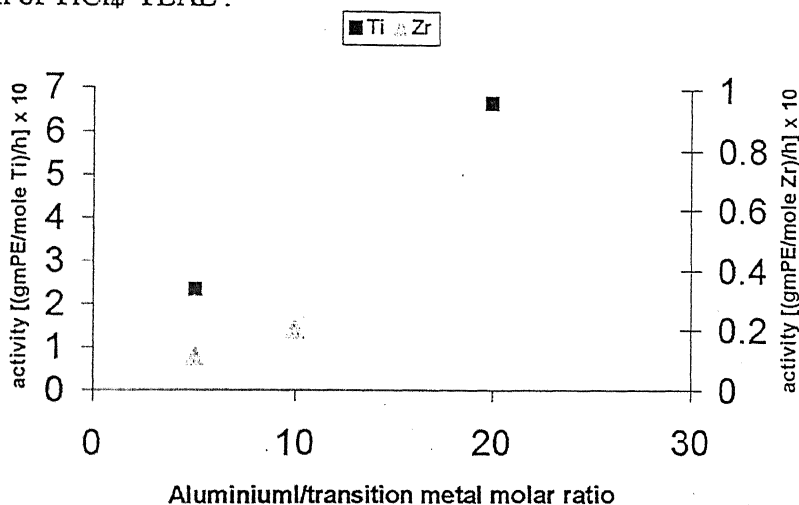
Fig. 6.2. Comparative Study of TiCl$_4$ and ZrCl$_4$ based polyethylene activity

Productivity of Polyethylene using Cp₂TiCl₂/ TEAL/ EAO as a Catalyst

Quality of Polymer using Cp$_2$TiCl$_2$/ TEAL/ EAO Catalyst seems to be better than TiCl$_4$/TEAL and ZrCl$_4$/TEAL due to uniformity in the size of polymer particle.Which is crumbly in nature because of this one can feel that molecular weight distribution is proper Activity of this catalyst comes around 3 x 10^4 gm polymer/ moles of Cp$_2$TiCl$_2$ which is not significant with the reported activity .Hence , lot of run is required such as change in the Al / Ti composition, effect of temperature, polymerization time, quality of solvent and impact of hydrogen to get the optimum activity. One can conceive ways to prepare metallocene /RAO catalysts whose activities would be far less sensitive to the transition metal to RAO ratios and have much lower requirements for [RAO].These synthesis are being studied in our laboratory.

Chapter 7

CONCLUSION and RECOMENDATIONS

CONCLUSION

All the evidence collected which clearly indicates that in order to obtain high cocatalyst activity by the " homogeneous and heterogeneous" Zieglar- Natta system based on TiCl$_4$/ TEAL , ZrCl$_4$ /TEAL and Cp$_2$TiCl$_2$ /TEAL/EAO complex .Cp$_2$TiCl$_2$ which is synthesized in lab is perfect in all the aspects but TEAL contains ether as an impurity. Hence, triethyl aluminum must be pure and satisfy mandatory structural requirement because it is also used as a primary material for synthesis of ethylaluminoxane otherwise it contain ether which is poisonous for polymerization We have hypothesized active species having Al-O-Al bond. Although this hypothesis seems to be appeared in our experimental results during the synthesis of aluminoxane. Further evidence are needed to draw significant conclusion. However, there are many other aspects to be clarified which enhance the better activity of TiCl$_4$/TEAL instead of ZrCl$_4$/TEAL and also for the catalytic activity of Cp$_2$TiCl$_2$/TEAL/EAO .These aspects could throw new light in the field of Zieglar-Natta and metallocene catalyst..

RECOMMENDATIONS:

1. During polymerization of ethylene using TiCl$_4$/TEAL and ZrCl$_4$/TEAL catalyst, one can check the effect of hydrogen , polymerization time , temperature , solvent and Al/Ti ratio more than 200 .This can help to optimize catalyst activity and yield of polymerization.

2. Same set of experiments can perform by taking TiCl4/MEAL (Trimethyl aluminum) instead of TiCl$_4$/TEAL and check the yield of polymerization.

3. The polymerization of Cp$_2$TiCl$_2$ /TEAL / EAO is very rough and yield is low compared to reported yield. Hence the optimization is required to get good polymer yield with specified characteristics. This can be possible by performing various run considering

Al/Ti ratio , temperature , time of polymerization , effect of solvent and also check the way to inject the catalyst into the reactor.

4. If one can perform the same polymerization reaction using $(MeCp)_2TiCl_2$ /TEAL and $(EtCp)_2TiCl_2$ /TEAL instead of Cp_2TiCl_2, then it is sure that the catalytic activity increases because electron donating ligands increases polymerization rate where the steric hindrance reduces it[1].

5. However, experimental difficulties arises from measuring very small quantity of hydrogen like 50 Nml so very efficient flow meter is recommended which can control this flow rate[2].

6. The order of additions of components in Ziegler-Natta polymerization is very important.The following order of addition is added with in a 10 min. interval between injection of reaction components in the sequence diluent, cocatalyst, catalyst and monomer which is slightly different than the order reported as diluent, monomer, cocatalyst and catalyst . One can check the activity of catalyst in both way and conclude which is more effective[3]

7. The polymerization activity of different catalysts can compared with Cp_2ZrCl_2, Cp_2ZrClH, Cp_2ZrMe_2,Et$[Ind]_2ZrCl_2$, $(IsoBuCp)_2TiCl_2$ and $(IsoBuCp)_2ZrCl_2$. using TEAL or MEAL or RAO as a cocatalyst[4].

8. Mass spectra and XRD of Cp_2TiCl_2 , ethylaluminoxane and polymer is also recommended because one can easily identify the molecular weight and structure of given compound.

9. Etheral complex of Triethylaluminum can purified by using active aluminum foil in which ether react with aluminum to form a solid complex and get pure form of tri ethyl aluminum[5].

10. The catalyst activity can be improved by removal of Lewis base like alkyl and aryl ethers and waters because they have a dramatic poisoning effect .The catalyst activity can be strongly affected also by changing the nature of both the alkyl and the cyclopentadienyl ligands of the IV th B transition metal complexes[6].

11. One can check the activity of Cp2TiCl2 / AlCl(R)$_2$: R= Me or Et, when calculated quantity of water is added to the polymerization system in a 3:1 Al/ H_2O molar ratio.

12. Various tests are recommended to get exact characteristic of polymer sample like DSC analysis , intrinsic viscocity, meant flow index, GPC analysis ,XRD, NMR spectra and the solubility of polymer into trichlorobenzene.

13. Kinetics study of polymerization using catalysts combination is very important for getting initiation, propogation and termination rate constant which will help to conclude the yield of polymer and also identify the involvement of catalyst in the polymerization reaction[7].

Referances

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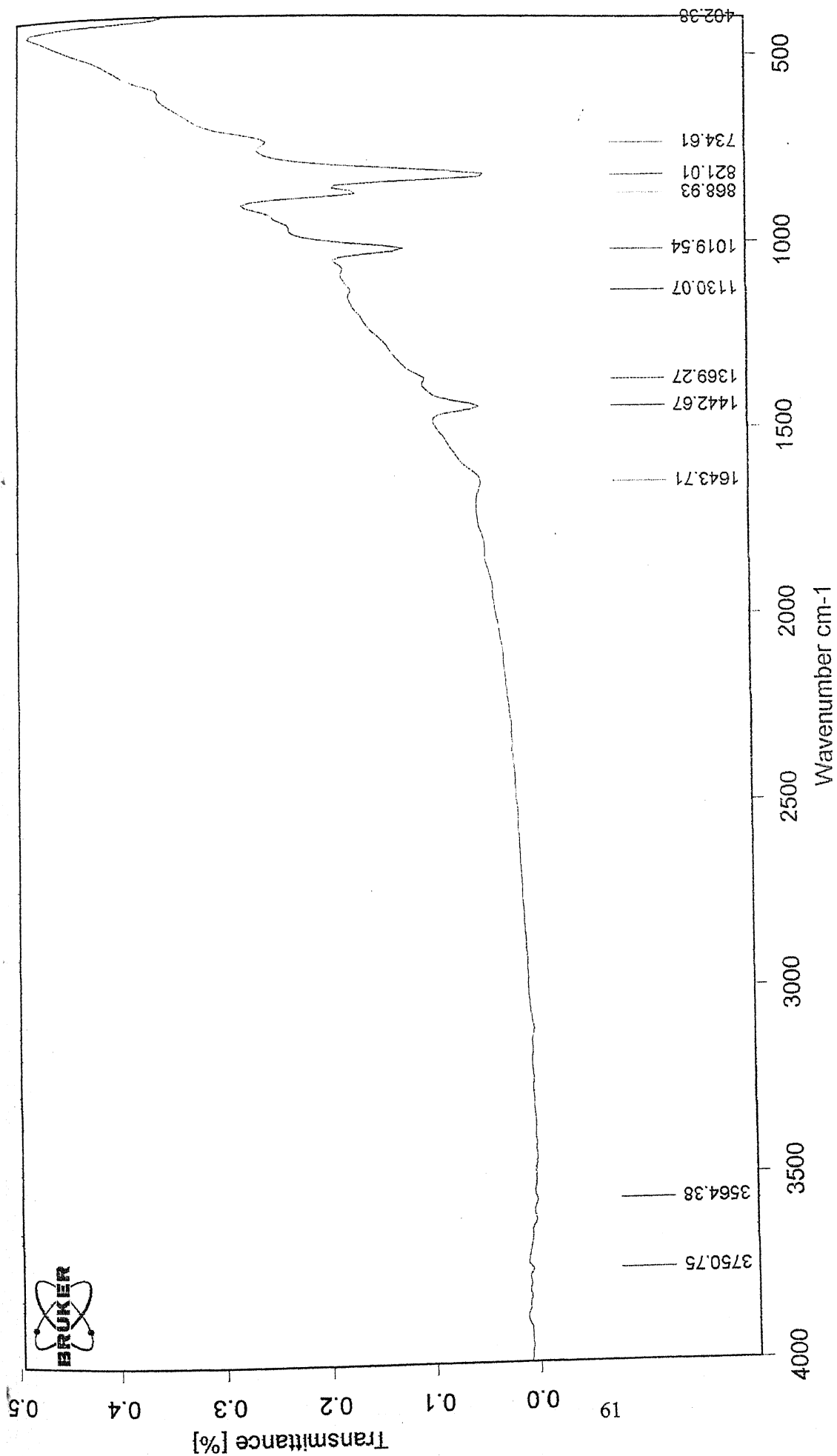
Fig . A1.1 FTIR of Cp₂TiCl₂ (Aldrich chemicals)

| C:\OPUS_NT\MEAS\CP2TICL2(W) | sample | sample for: | 10/09/2002 |

Seite 1 von 1
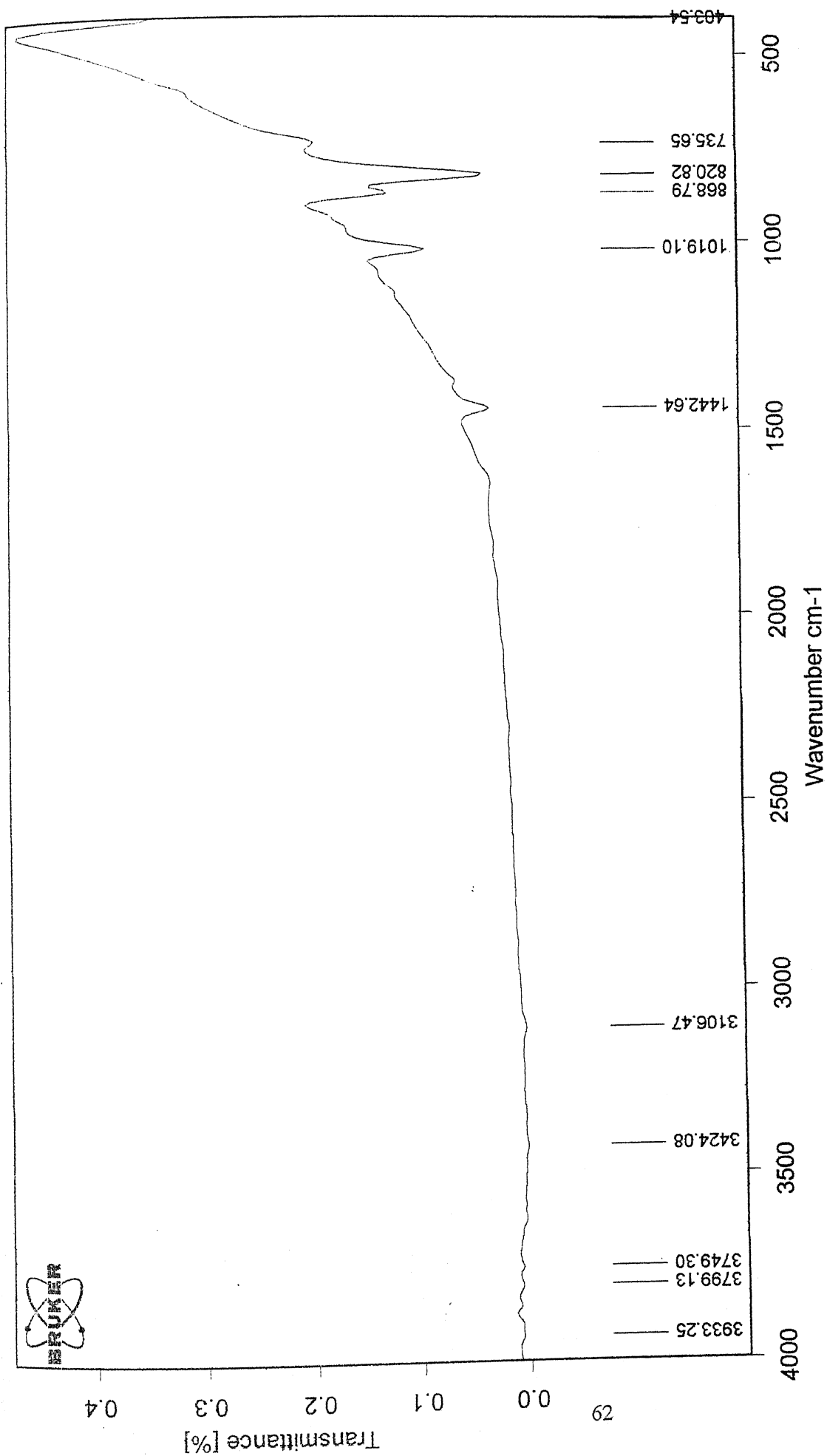
Fig. A1.2 FTIR of Cp₂TiCl₂ (Synthesized in Lab)

C:\OPUS_NTMEAS\CP2TICL2-C.0   sample   sample form   10/09/2002

Seite 1 von 1
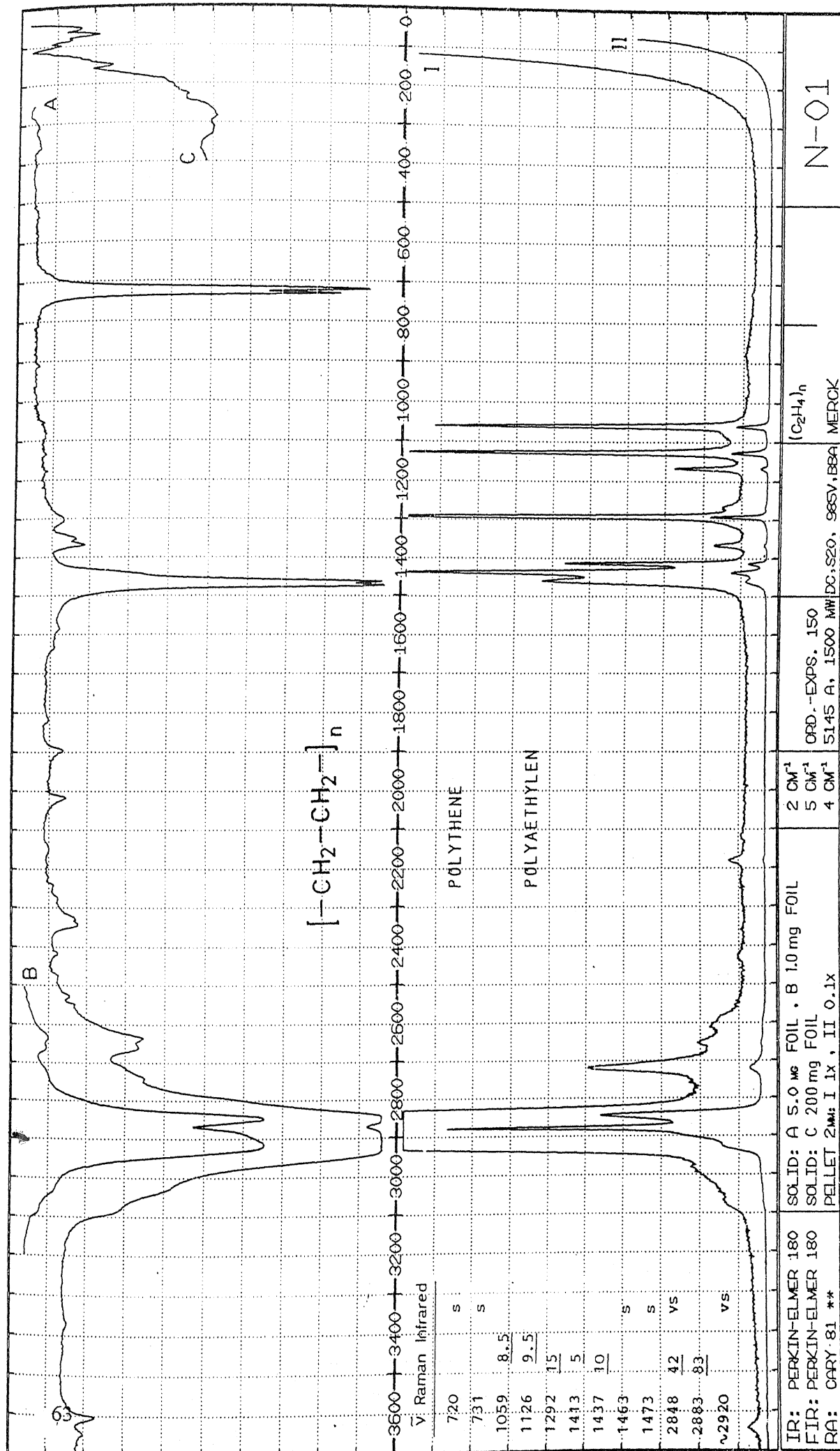
Fig. A1.3　FTIR of Polyethylene (Reported)
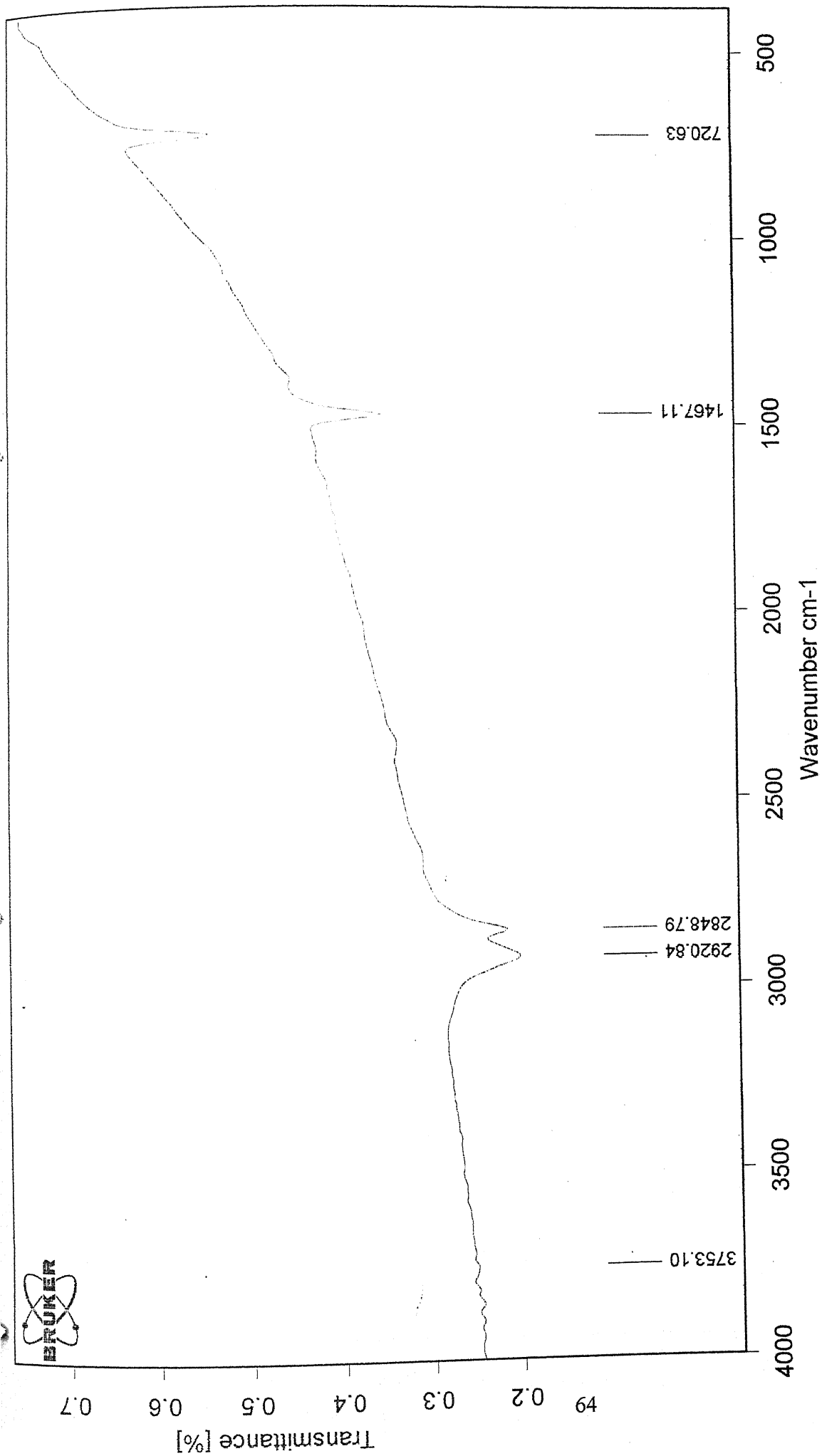
Fig . A1.3   FTIR of Polyethylene (GAIL Sample)

Seite 1 von 1

| C:\OPUS_NT\MEAS\GAIL.1 | sample | sample form | 22/10/2002 |
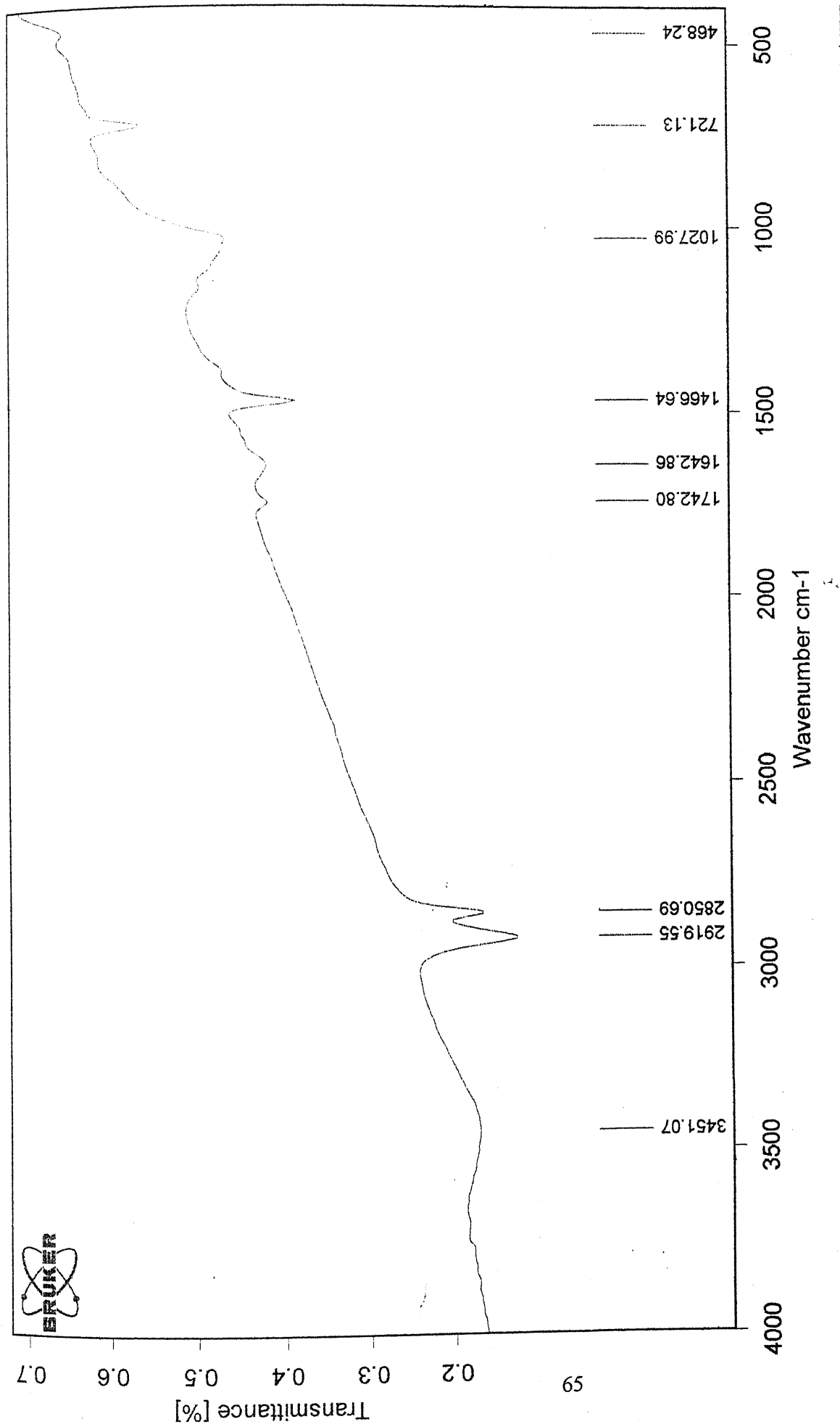
Fig . A1.3   FTIR of Polyethylene (PV-III)

Seite 1 von 1

13/08/2002

C:\OPUS_NT\MEAS\PV-III.0   sample   sample form
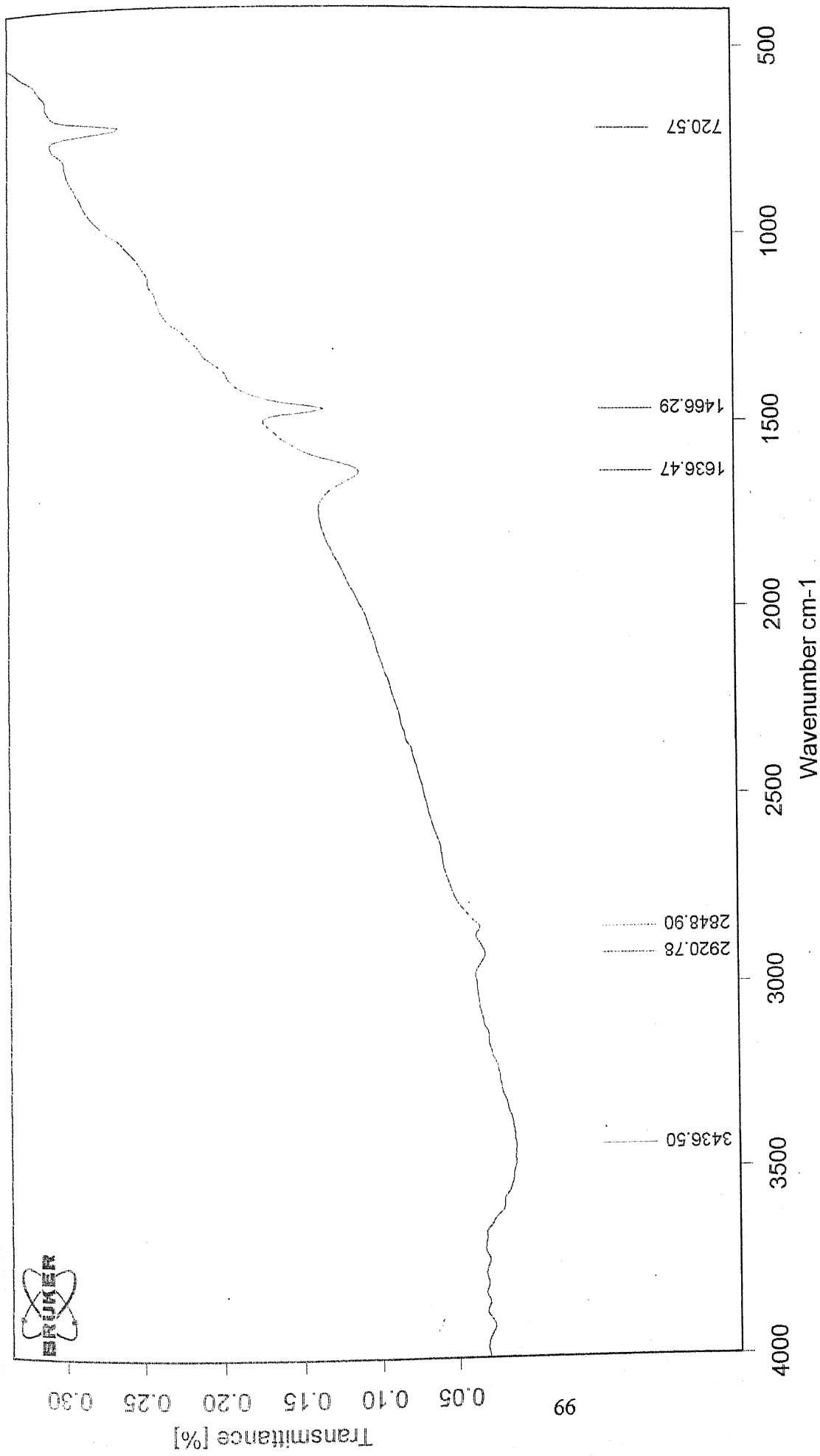
Fig . A1.3   FTIR of Polyethylene (PV-IV)

	sample form

C:\OPUS_NT\MEAS\PV-IV.0	sample		23/08/2002

Seite 1 von 1
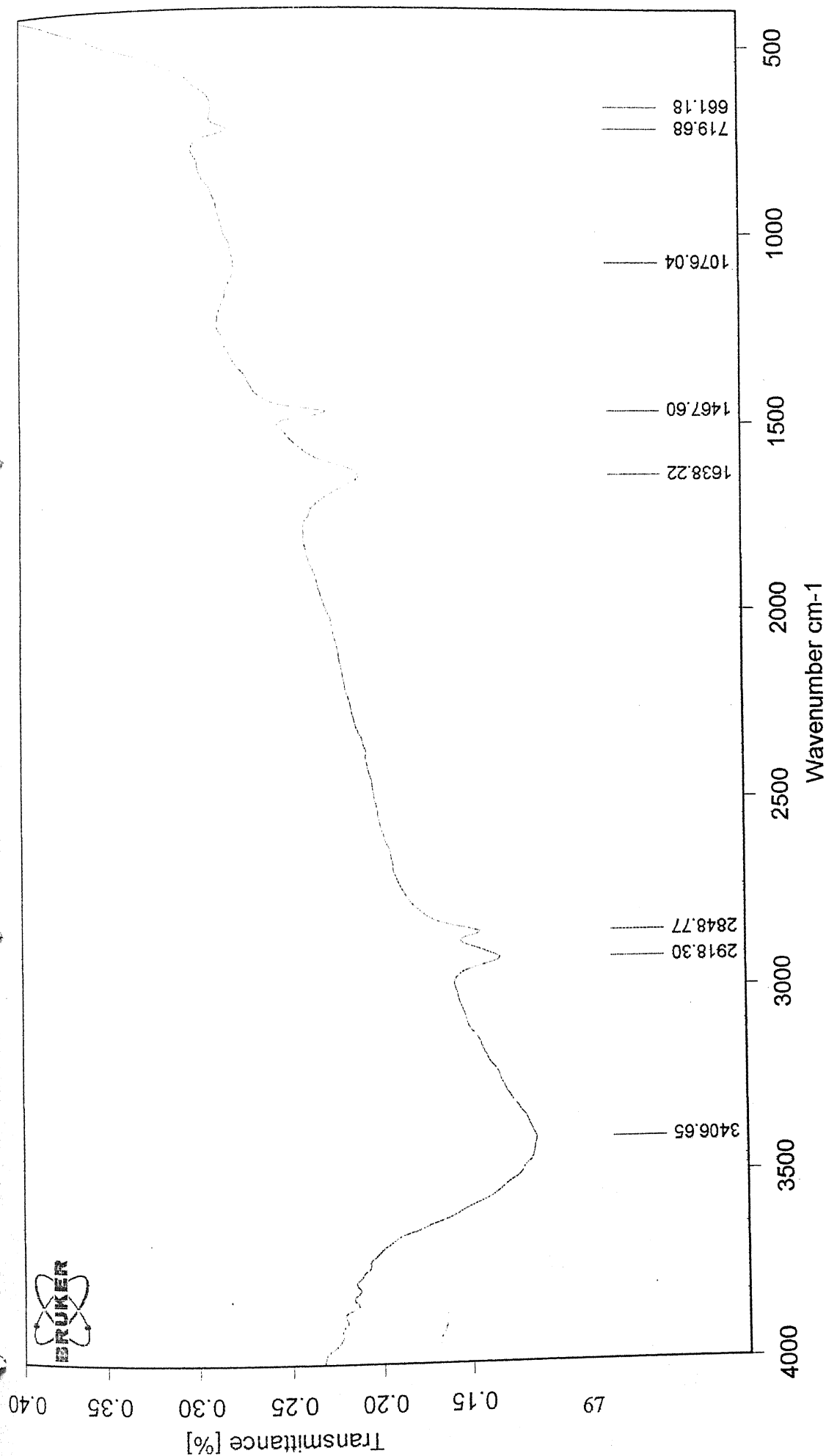
Fig. A1.3   FTIR of Polyethylene (PV-VI)

Seite 1 von 1

| C:\OPUS_NT\MEAS\PV-VI.0 | sample | sample form | 18/10/2002 |
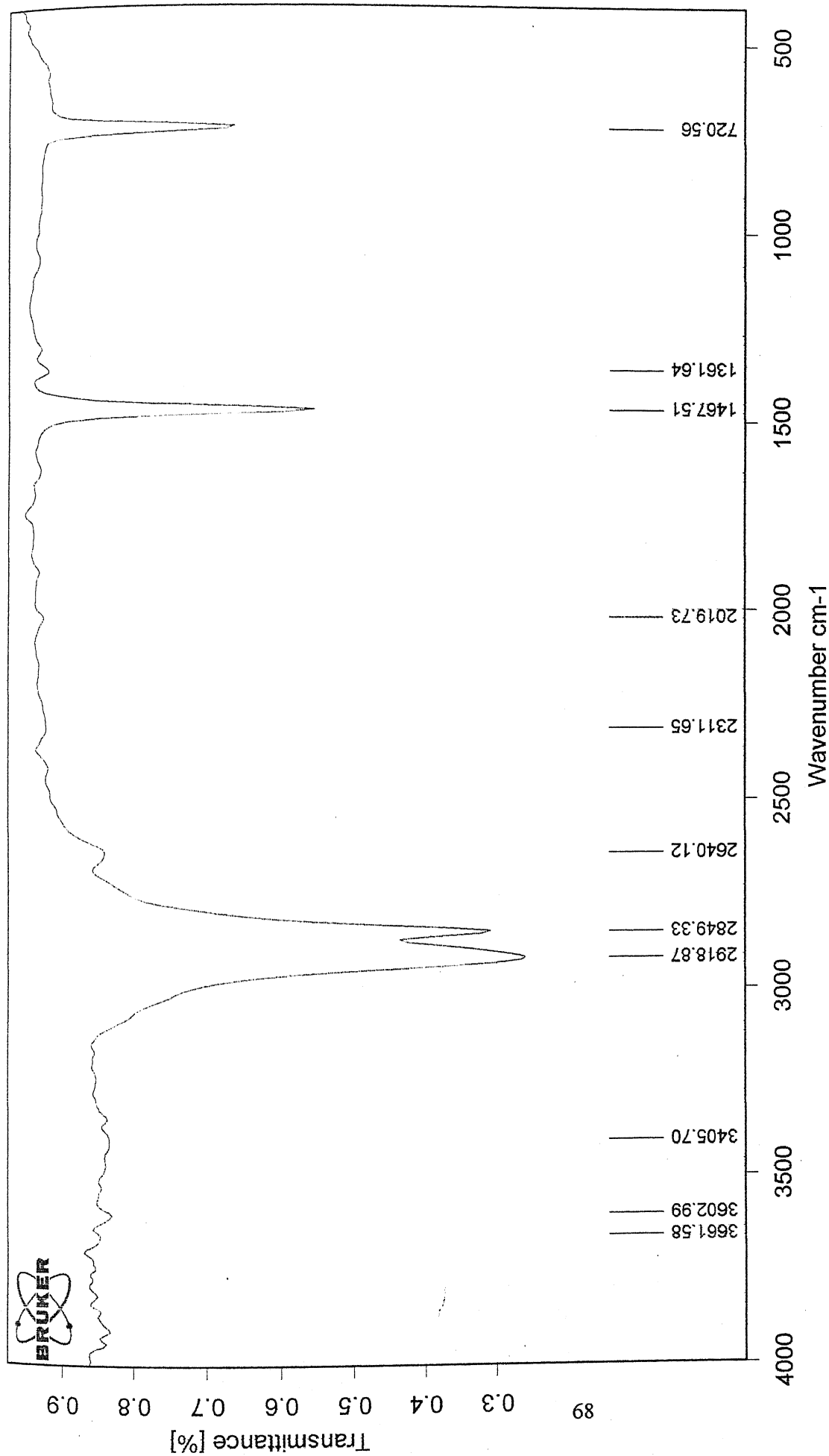
Fig . A1.3   FTIR of Polyethylene (PV-IX)

Seite 1 von 1

| C:\OPUS_NT\MEAS\PV-9.0 | sample | sample form | 21/10/2002 |
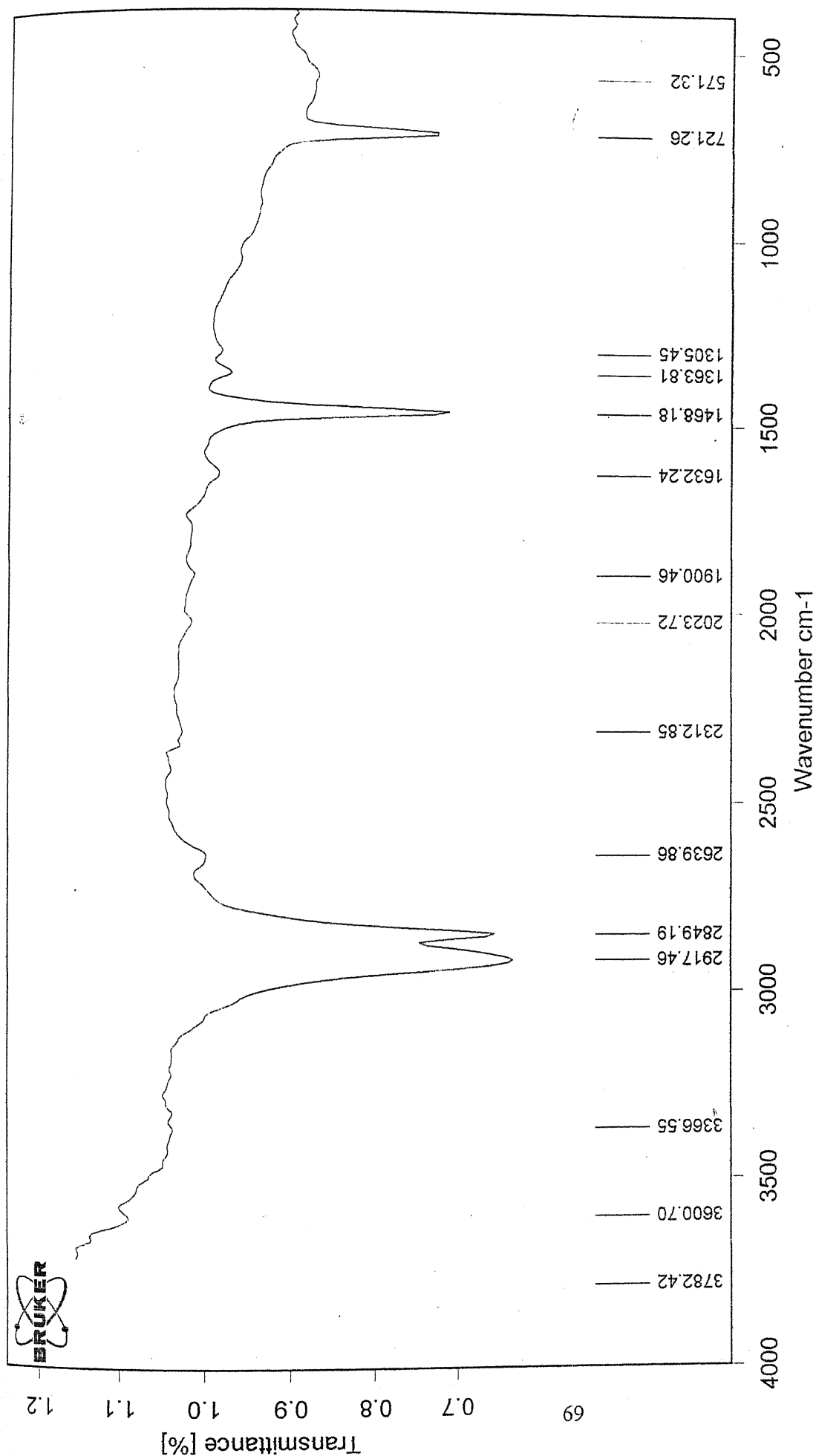
Fig. A1.9   FTIR of Polyethylene (PV-X)

Seite 1 von 1
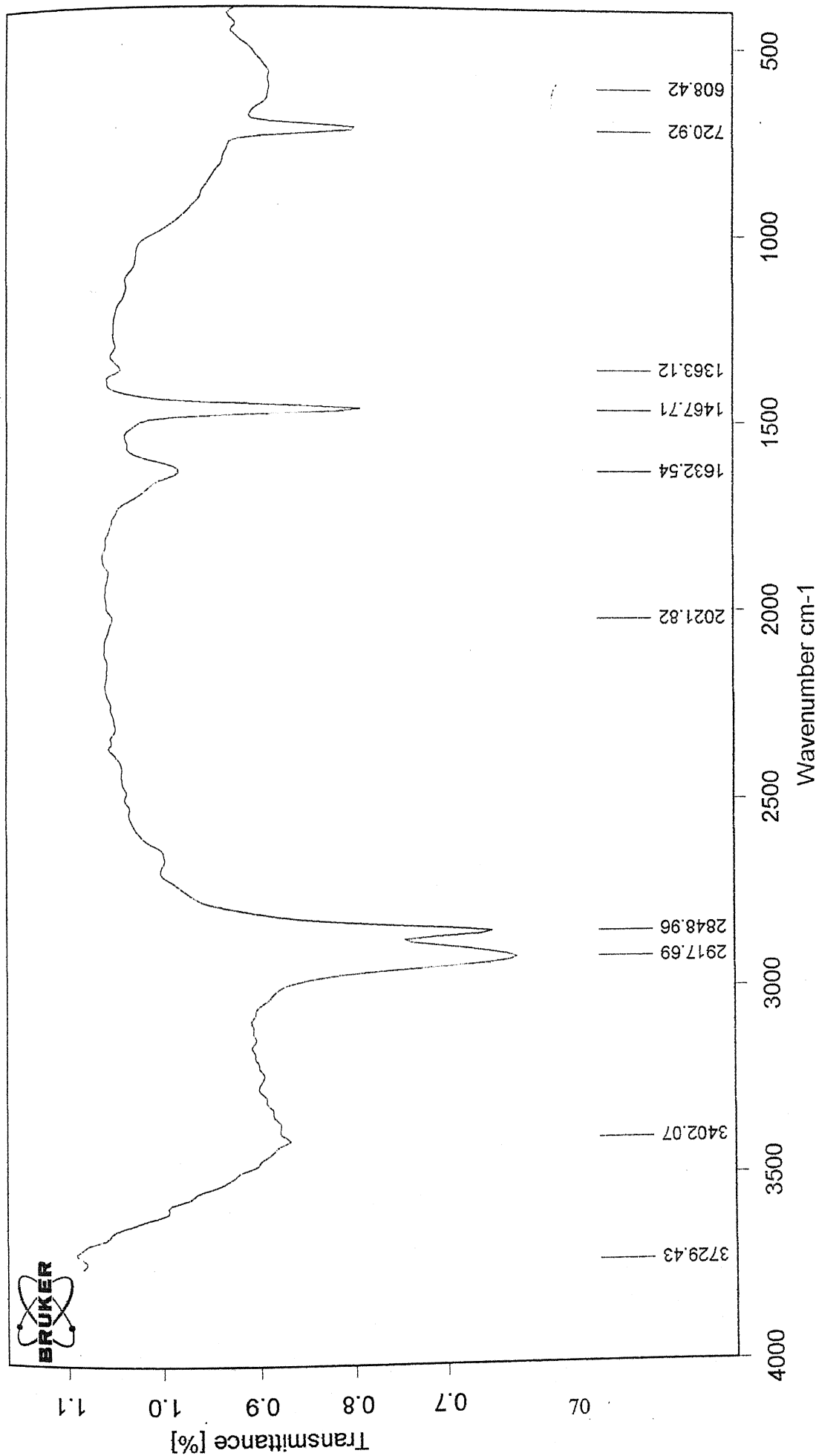
| C:\OPUS_NT\MEAS\PV-10.0 | sample | sample form | 21/10/2002 |

Fig . A1.10   FTIR of Polyethylene (PV-XI)

Seite 1 von 1
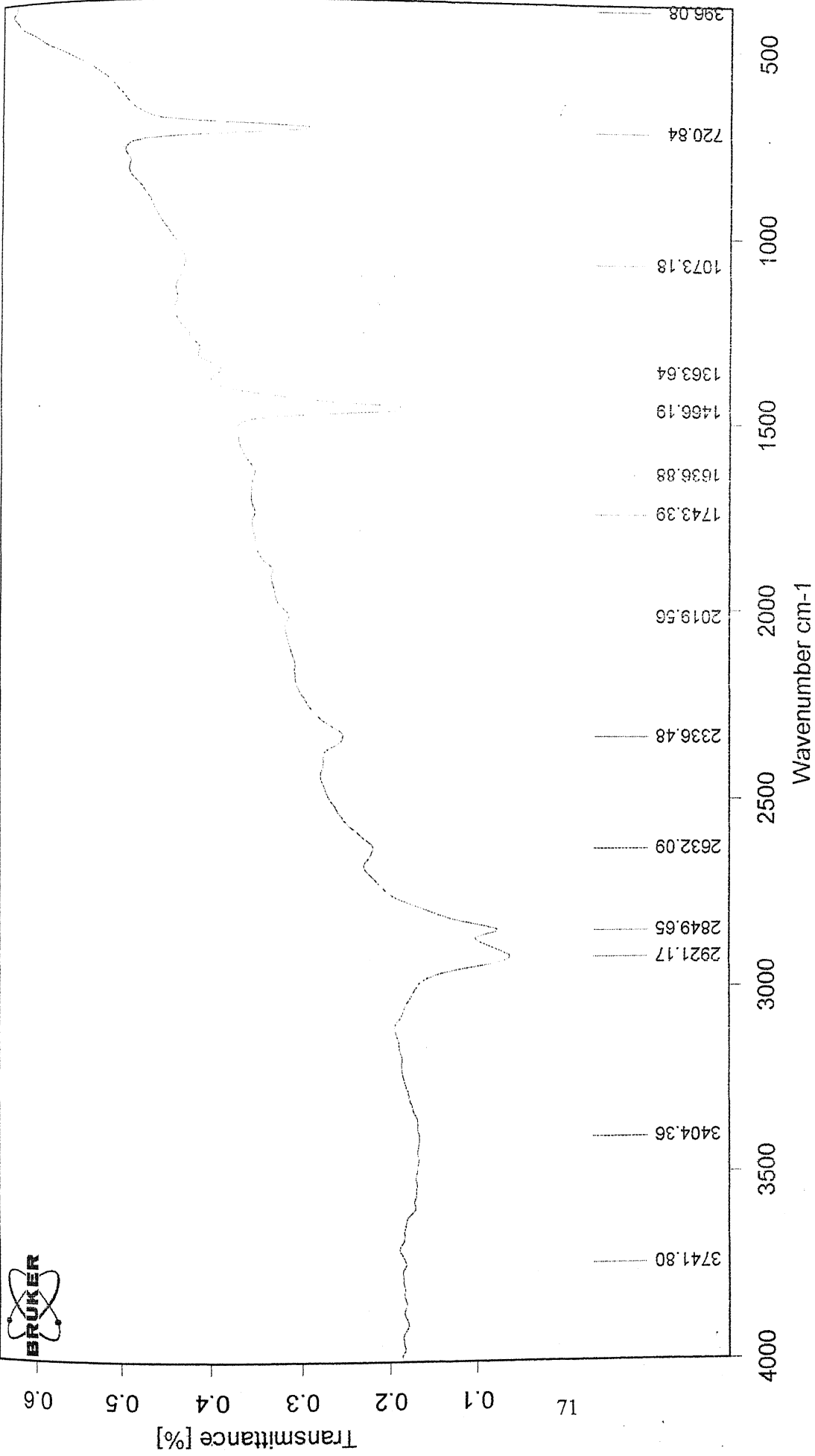
C:\OPUS_NT\MEAS\PV-11.0   sample   sample form   21/10/2002

Fig . A1.11   FTIR of Polyethylene (PV-XII)

Seite 1 von 1
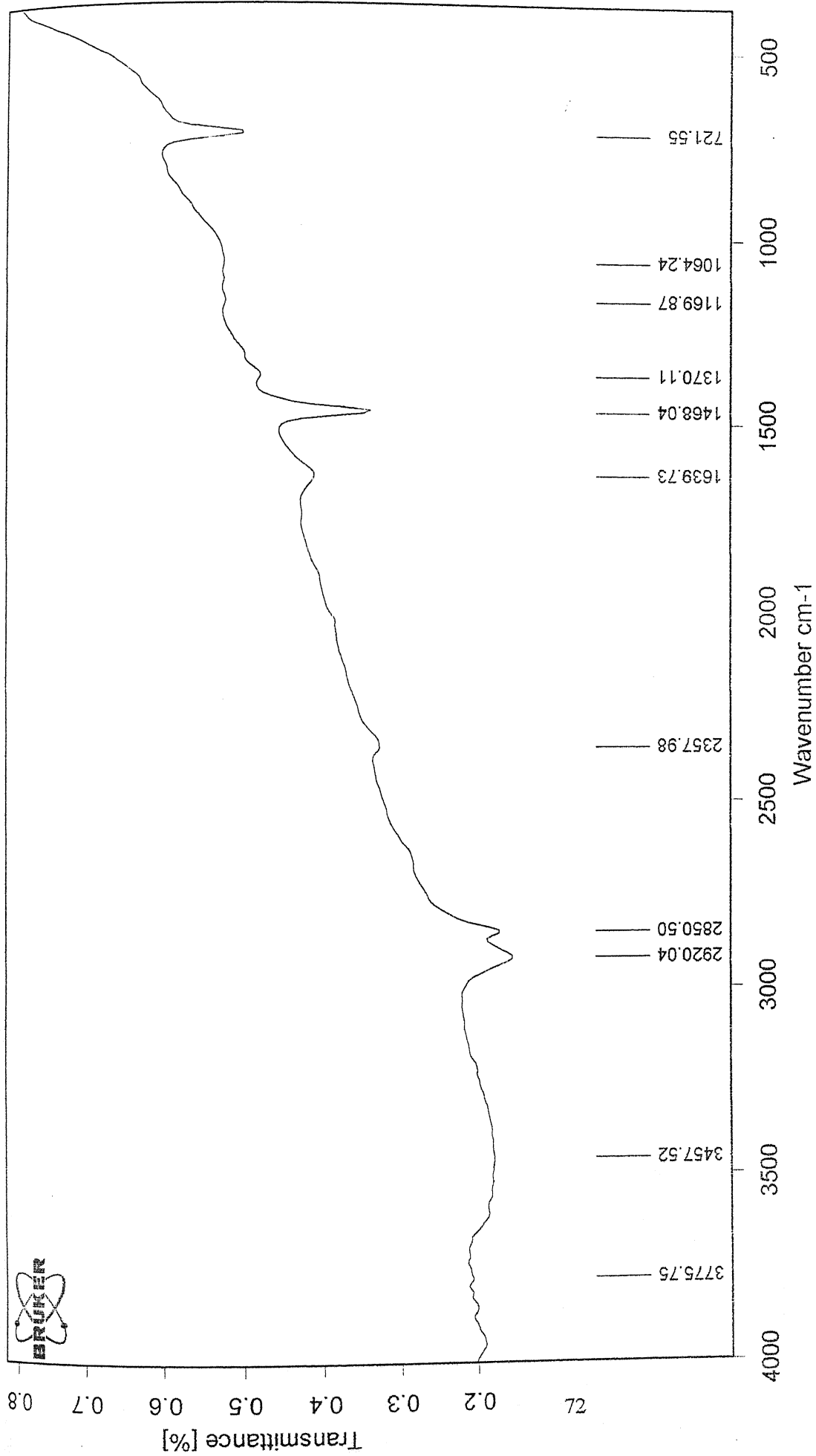
Fig . A1.12 FTIR of Polyethylene (PV-XIII)

Seite 1 von 1

C:\OPUS_NT\MEAS\PV\13.0	sample	sample form	22/10/2002

Peaks (cm-1): 3775.75, 3457.52, 2920.04, 2850.50, 2357.98, 1639.73, 1468.04, 1370.11, 1169.87, 1064.24, 721.55

Axes: Transmittance [%] (0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 72) vs Wavenumber cm-1 (4000, 3500, 3000, 2500, 2000, 1500, 1000, 500)
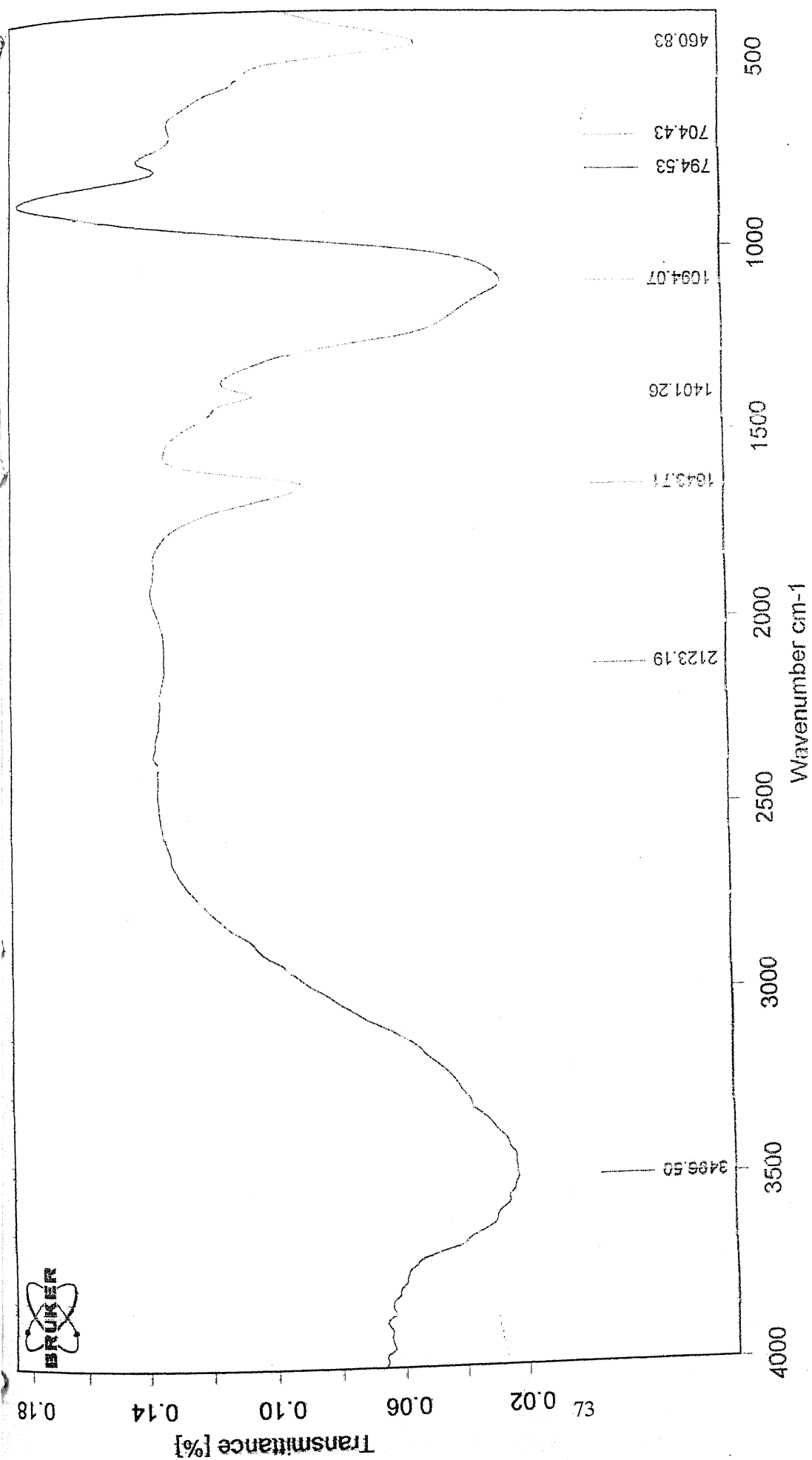
Fig AL.3 FTIR of Silica (Aldrich chemicals)

C:\OPUS_NT\MEAS\SiO2.0   sample   sample form

06/09/2002

Seite 1 von 1
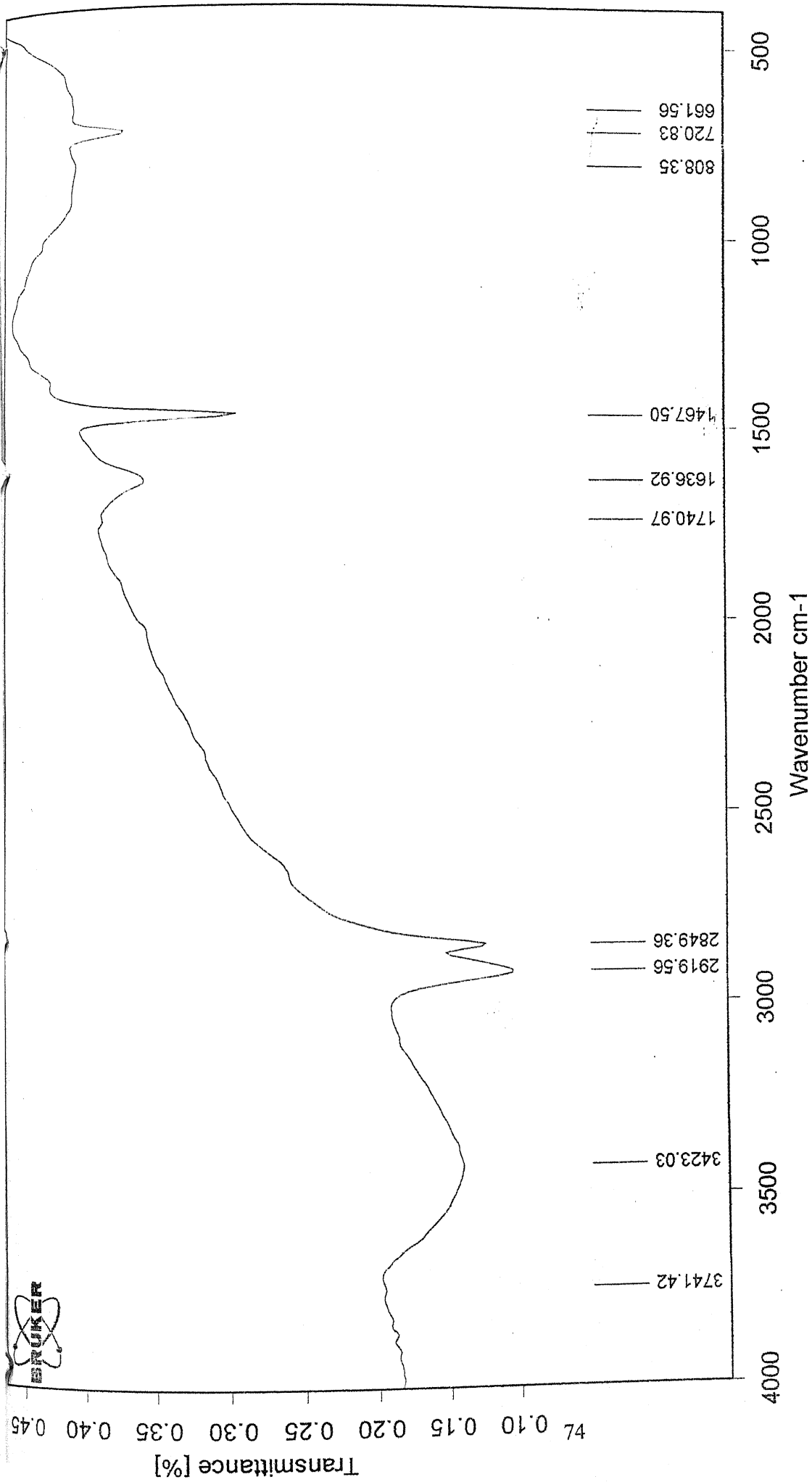
Fig. A1.14 FTIR of Polyethylene (PV-XV)

| C:\OPUS_NT\MEAS\PV-15.0 | sample | sample form | 23/10/2002 |

Seite 1 von 1
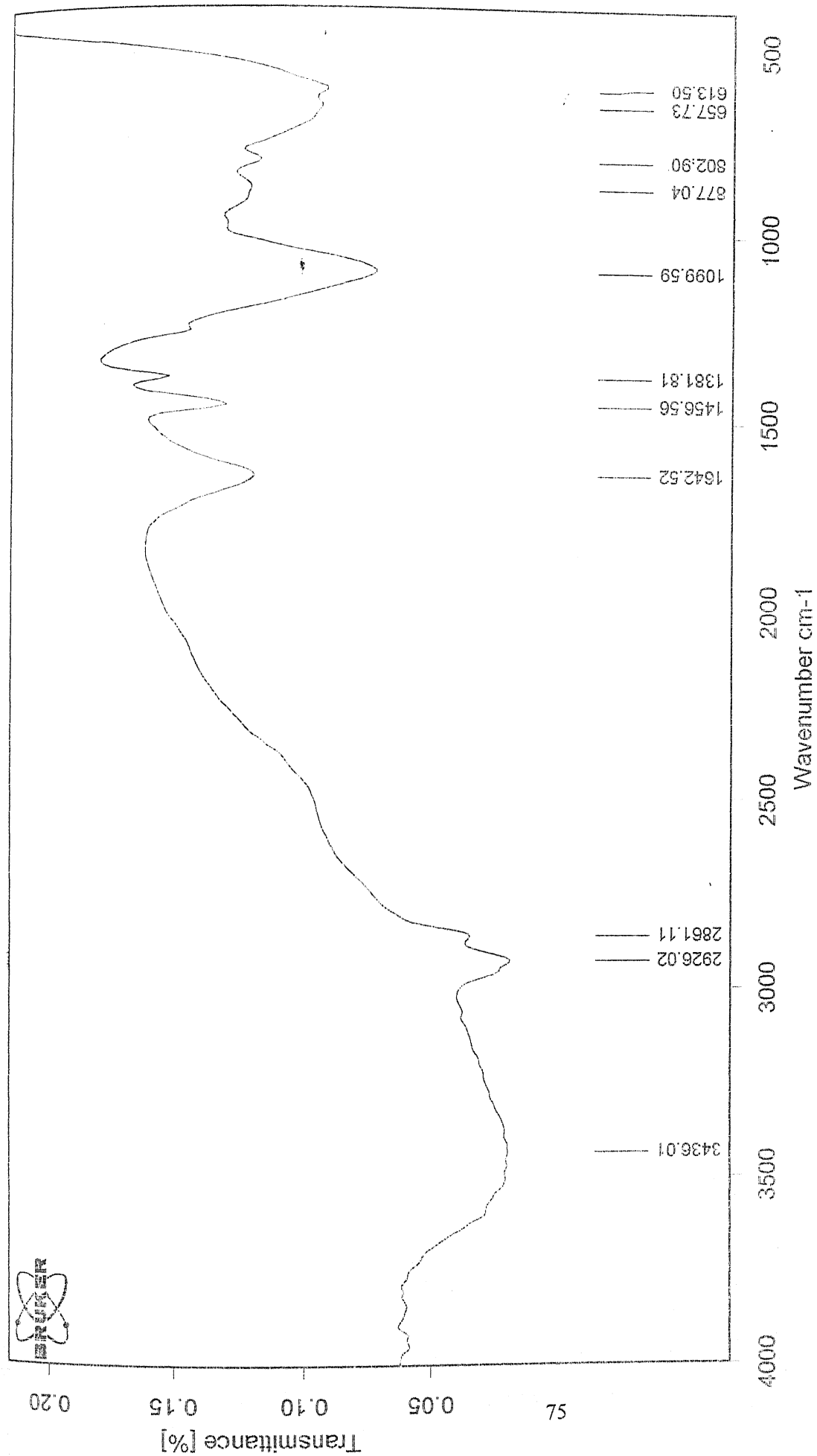
Fig. A1.15   FTIR of Ethyl Aluminoxane(EAO I)

Seite 1 von 1

| C:\OPUS_NT\MEAS\TEA-I.0 | sample | sample form | | 05/09/2002 |
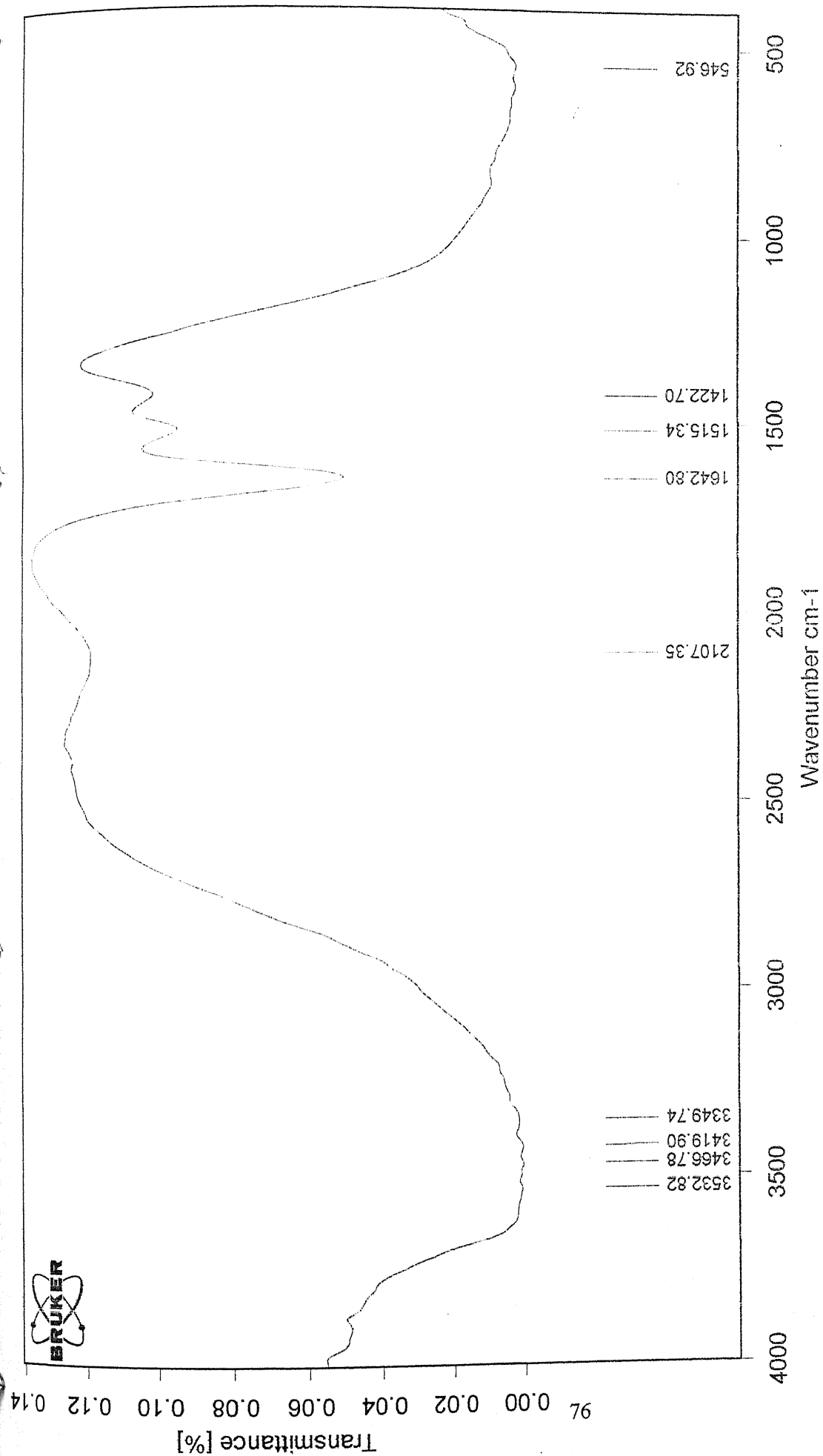
Fig. A1.16 FTIR of Ethyl Aluminoxane (EAO II)

Seite 1 von 1

C:\OPUS_NT\MEAS\EAO-II.0   sample   sample form   17/09/2002

XRD - EAO-II

Sweep 3.0 °/min Range (CPM) 5K Time Constant (s) 10.0

Target Cu 20 mA 30 kV

Datafile C:\xray-data\Xx101806.txt Run on 18 Oct 2002 at 12:45

X-Ray Laboratory, ACMS, IIT Kanpur

ANGLE IN DEGREES

INTENSITY %

78
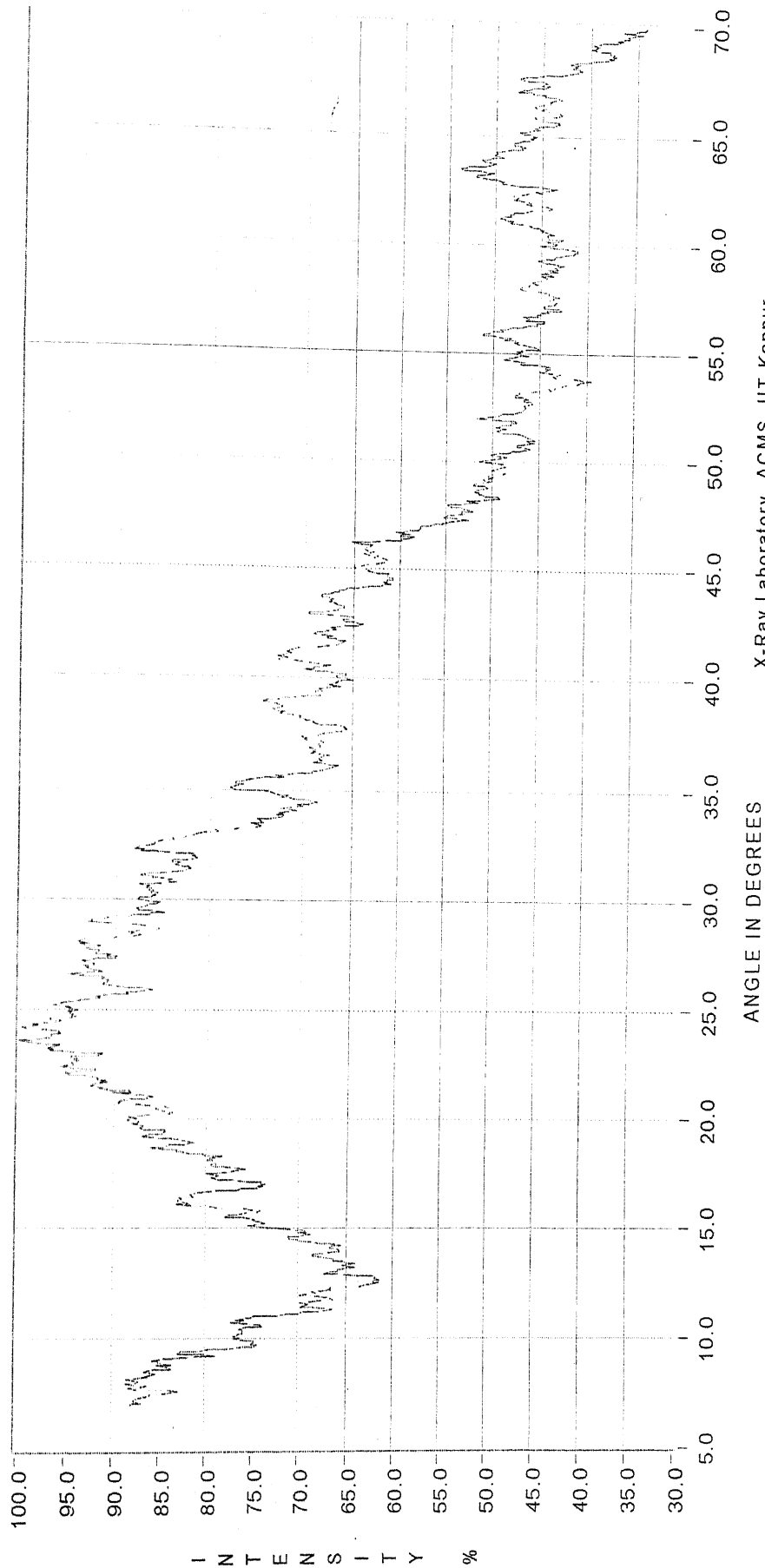
XRD - EAO-I-Repeat

Sweep 3.0 °/min   Range (CPM)   5K   Time Constant (s)   10.0

Target Cu   20 mA   30 kV

Datafile C:\xray-data\Xx102202.txt   Run on 22 Oct 2002   at   14:56
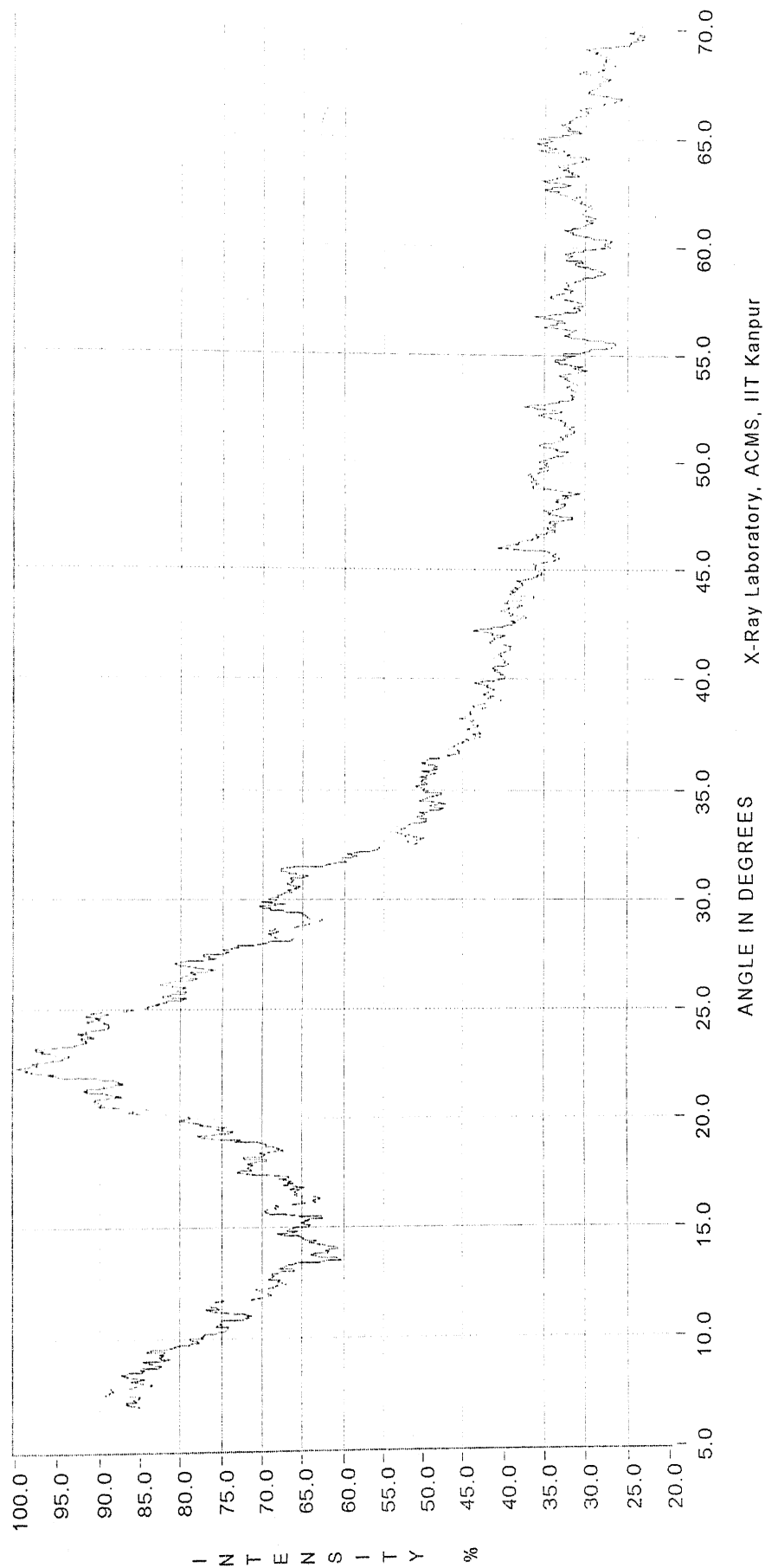
X-Ray Laboratory, ACMS, IIT Kanpur

ANGLE IN DEGREES

INTENSITY %

77

XRD-EAO-II

| Sweep | 3.0 | °/min | Range (CPM) | 5K | Time Constant (s) | 10.0 |

| Target | Cu | | 20 | mA | 30 | kV |

Datafile C:\xray-data\xx101806.txt   Run on 18 Oct 2002   at 12:

% Intensity	Angle°	d Å
77.51	15.56	5.694507
83.11	16.22	5.466049
78.65	17.37	5.104169
79.05	17.98	4.933941
79.05	17.98	4.933941
86.28	18.63	4.762037
86.09	19.24	4.613787
88.68	19.89	4.463394
89.32	20.75	4.281119
92.47	21.50	4.132406
94.68	22.11	4.020795
94.20	22.46	3.958480
100.00	23.57	3.774847
98.61	24.17	3.681827
96.15	25.18	3.536792
94.51	26.59	3.352350
92.85	26.89	3.315366
92.73	28.00	3.186650
92.45	29.06	3.070304
87.81	29.61	3.016795
87.53	30.01	2.977213
86.89	30.47	2.933949
87.48	31.07	2.878252
83.23	31.63	2.829090
88.14	32.28	2.773193
77.47	35.20	2.549493
68.12	36.36	2.470892
69.26	36.76	2.444734
69.68	37.37	2.406574
74.53	38.98	2.310710
68.97	40.54	2.225258
73.18	41.04	2.199110
69.10	42.05	2.148738
69.62	43.01	2.103124
68.25	43.76	2.068559
64.56	45.07	2.011464
62.67	45.83	1.980051
63.08	46.08	1.969816
58.87	46.68	1.945716
55.18	47.44	1.916482
54.23	47.94	1.897521
51.83	48.65	1.871657
51.52	50.06	1.822191
51.44	52.07	1.756342
50.73	55.90	1.644822
53.70	63.50	1.464958

79

XRD - EAO-II (after 5hrs heating at 50C)

Sweep 3.0 °/min   Range (CPM) 5K   Time Constant (s) 10.0

Target Cu   20 mA   30 kV

Datafile   C:\xray-data\Xx102203.txt   Run on 22 Oct 2002   at 15:24

X-Ray Laboratory, ACMS, IIT Kanpur

ANGLE IN DEGREES

INTENSITY %

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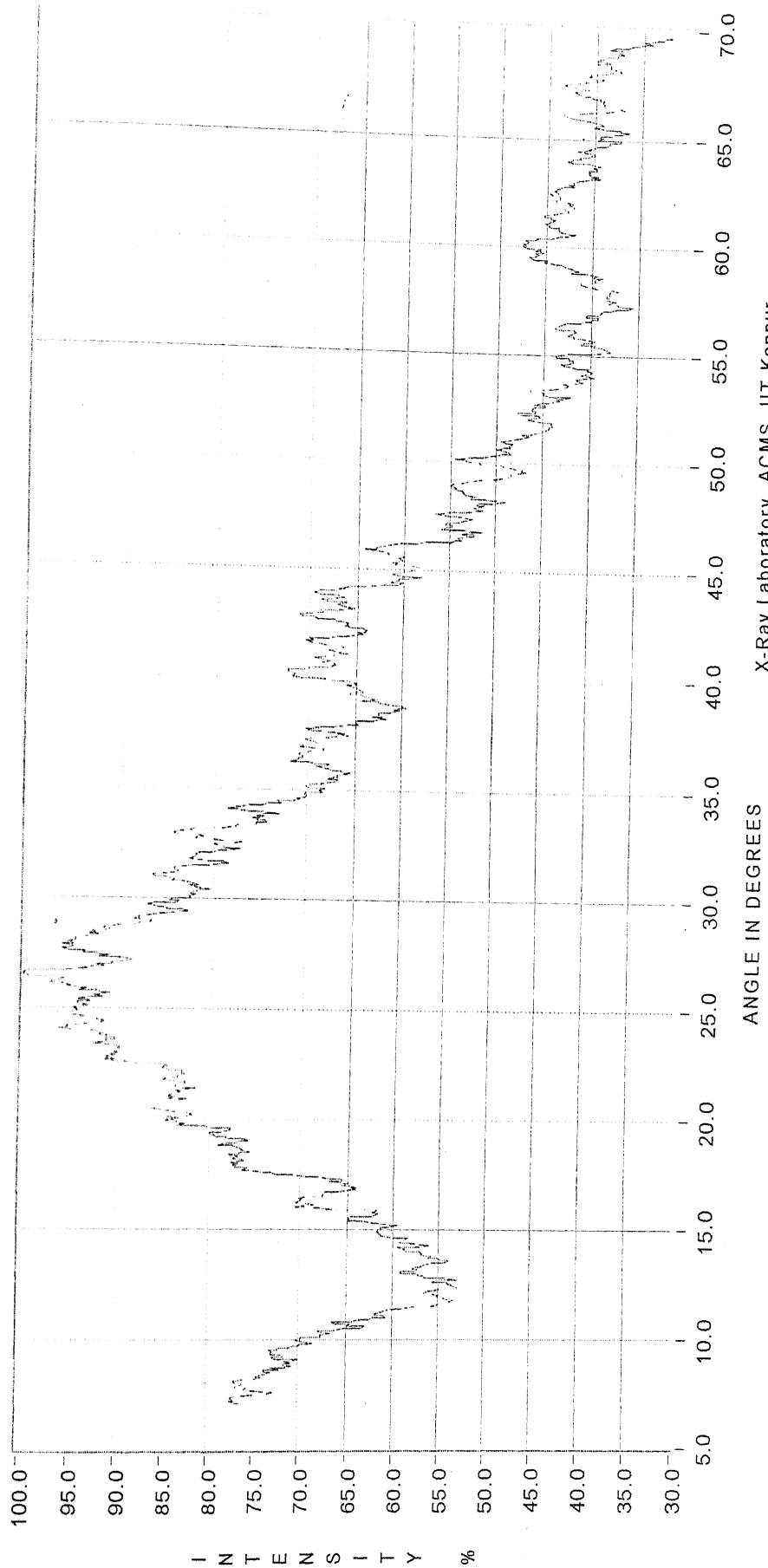
Appendix 2
NMR spectra

Date : Thu Jun 6 12:51:59 2002

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Comment	: CP-II-1H
SliceHistory	:
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SAMPO	: 32768 points
FREQU	: 7993.6 Hz
FILTR	: 4000 Hz
DELAY	: 50.0 usec
DEADT	: 71.8 usec
INTVL	: 125.1 usec
TIMES	: 16 times
DUMMY	: 0 times
PD	: 2.9007 sec
ACQTM	: 4099.2769 msec
PREDL	: 10.00000 msec
INIWT	: 0.5000 msec
RESOL	: 0.24 Hz
PW1	: 6.35 usec
OBNUC	: 1H
OBFRQ	: 399.65 MHz
OBSET	: 13430.00 Hz
RGAIN	: 17
SCANS	: 16 times
SLVNT	: CDCL3
SPINNING	: 13 Hz
TEMP	: 25.0 C

Peaks: 0.0000, 1.1881, 1.5603, 2.1033, 6.5236, 7.1954

Integrations: 4.56, 1.00, 5.19, 1.38, 61.13, 1.85
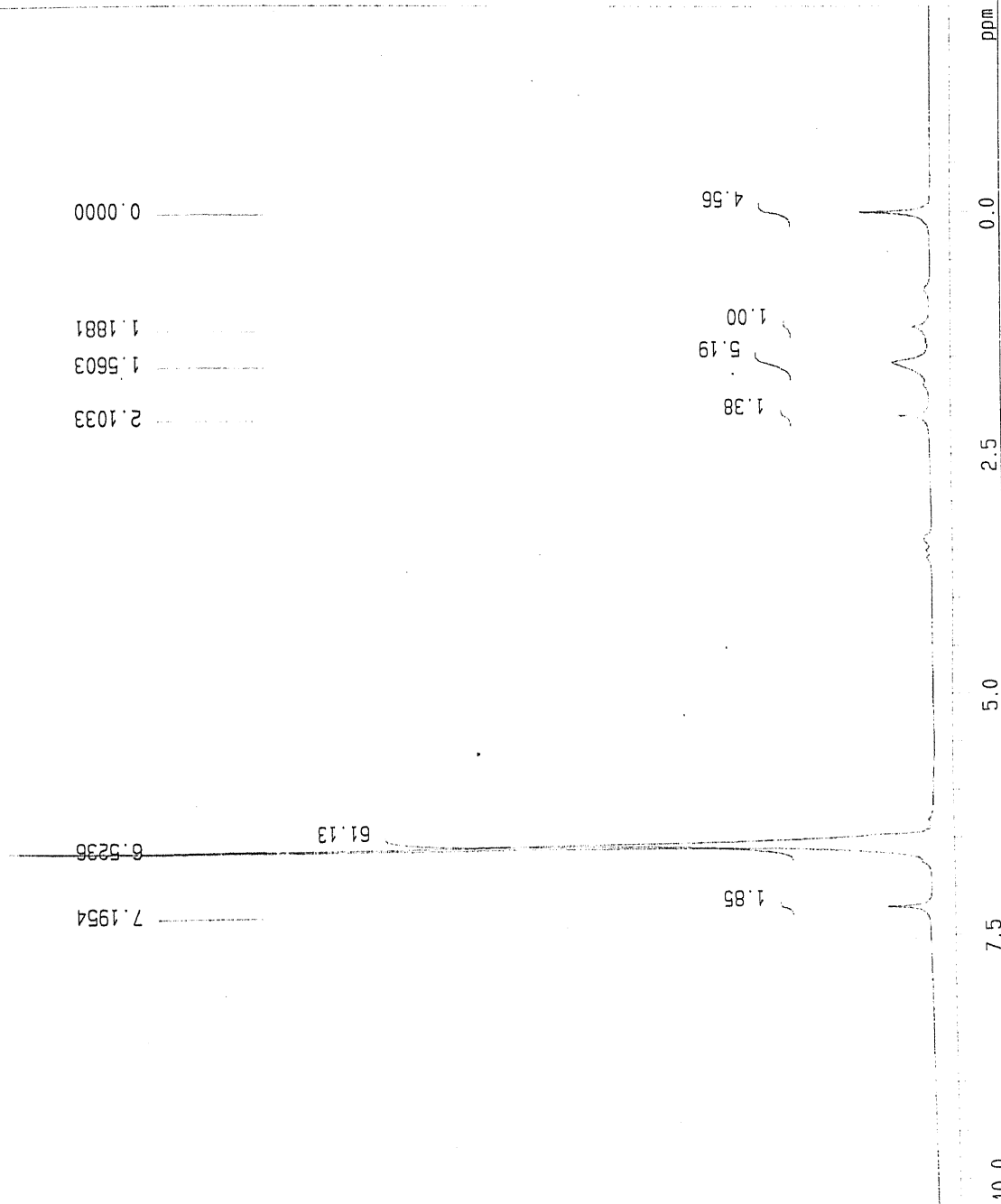
Fig. A2.1
NMR of Cp$_2$TiCl$_2$
(Synthesized in Lab)

81

CP2TICL2-1H

Date : Mon Aug 5 08:54:52 2002

FileName	:	CP2TICL2-1H.nmdata
Comment.	:	CP2TICL2-1H
SliceHistory	:	
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DEADT		71.8 usec
INTVL		125.1 usec
TIMES		16 times
DUMMY		1 times
PD		2.9007 sec
ACQTM		4099.2769 msec
PREDL		10.00000 msec
INIWT		1000.0000 msec
RESOL		0.24 Hz
PW1		6.35 usec
OBNUC		1H
OBFRQ		399.65 MHz
OBSET		13430.00 Hz
RGAIN		19.
SCANS		16 times
SLVNT	:	CDCL3
SPINNING		11 Hz
TEMP		20.8 C

Fig. A2.2
NMR of Cp₂TiCl₂
Commercial Sample
from Aldrich

0.0421

1.2253
1.5969

2.3304

6.3381
6.3442
6.3509
6.5041
6.5194
6.5371
6.5425
6.5694
6.6011
6.6335
6.6567
6.7842
6.7909
7.2132
7.2400

0.06

0.18
2.10

0.04

26.87
0.10
0.11
1.00

ppm

0

5

10

82

Date : Wed Aug 21 16:00:59 2002

FileName   : CPZNI-1H.nmdata
Comment   : CP-ZN-I-1H
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DEADT   71.8 usec
INTVL   125.1 usec
TIMES   16 times
DUMMY   1 times
PD   2.9007 sec
ACQTM   4099.2769 msec
PREDL   10.00000 msec
INIWT   1000.0000 msec
RESOL   0.24 Hz
PW1   6.35 usec
OBNUC   1H
OBFRQ   399.65 MHz
OBSET   13300.00 Hz
RGAIN   22

SCANS   16 times

SLVNT   CDCL3
SPINNING   13 Hz
TEMP   25.0 C

Fig . A2.3
NMR of Cp₂ZrCl₂
Commercial Sample
from Aldrich

1.2314
1.4114
1.5335

3.4641

4.6046
5.2782
6.0623
6.0690
6.0757
6.2137
6.2295
6.2539
6.2759
6.2863
6.2881
6.2991
6.3223
6.3351
6.3570
6.4687
6.4705
6.4803
6.4962
6.5011
6.5078
7.2382
7.2400

0.24
1.00

0.16

0.24

0.02

30.64   0.14

1.31

ppm
0.0
2.5
5.0
7.5
10.0

83

Date : Wed Aug 21 16:00:59 2002

FileName   : CPZNI-1H.nmdata
Comment   : CP-ZN-I-1H
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DEADT   71.8 usec
INTVL   125.1 usec
TIMES   16 times
DUMMY   1 times
PD   2.9007 sec
ACQTM   4099.2769 msec
PREDL   10.00000 msec
INIWT   1000.0000 msec
RESOL   0.24 Hz
PW1   6.35 usec
OBNUC   1H
OBFRQ   399.65 MHz
OBSET   13400.00 Hz
RGAIN   22

SCANS   16 times

SLVNT   CDCL3
SPINNING   13 Hz
TEMP   25.0 C

Fig. A2.3
NMR of Cp2ZrCl2
Commercial Sample
from Aldrich

1.2314
1.4114
1.5335

3.4641

4.6046
5.2782
6.0623
6.0690
6.0757
6.2137
6.2295
6.2539
6.2759
6.2863
6.2881
6.2991
6.3223
6.3351
6.3570
6.4687
6.4705
6.4803
6.4962
6.5011
6.5078
7.2382
7.2400

0.24
1.00

0.16

0.24

0.02

0.14
30.64

1.31

10.0   7.5   5.0   2.5   0.0   ppm

83

Date : Fri Jun 7 16:12:20 2002

FileName   : TEAL-I-1H.nmdata
Comment   : TEAL-I-1H
SliceHistory :
EXMODE   : non

POINT   32768 points
SAMPO   32768 points
FREQU   7993.6 Hz
FILTR   4000 Hz
DELAY   50.0 usec
DEADT   71.8 usec
INTVL   125.1 usec
TIMES   16 times
DUMMY   1 times
PD   2.9007 sec
ACQTM   4099.2769 msec
PREDL   10.00000 msec
INIWT   1000.0000 msec
RESOL   0.24 Hz
PW1   6.35 usec
OBNUC   1H
OBFRQ   399.65 MHz
OBSET   134300.00 Hz
RGAIN   6

SCANS   16 times

SLVNT   CDCL3
SPINNING   13 Hz
TEMP   26.4 C

Fig . A2.4
NMR of TEAL I
Synthesize in Lab

-0.3209
-0.3008
-0.2807
-0.2599
-0.2508
-0.2294
-0.2166
-0.2080
-0.1965
-0.1757
-0.1556
-0.0031
0.8372
0.8830
0.8976
0.9178
0.9281
0.9379
0.9489
0.9574
0.9690
1.0502
1.0703
1.1936
1.2107
1.2168
1.2277
1.2345
1.2454
1.2522
1.3028
1.3052
1.3205
3.7393
3.7570
3.7747
3.7924

7.0795
7.0960
7.1442
7.1625
7.2400

5.27

1.00

-0.04

1.68

0.01

84

ppm

0   2   4   6   8   10

Date : Fri Jun 7 16:12:20 2002

FileName	:	TEAL-I-1H.nmdata
Comment	:	TEAL-I-1H
SliceHistory	:	
EXMODE	:	non

POINT	32768	points
SAMPO	32768	points
FREQU	7993.6	Hz
FILTR	4000	Hz
DELAY	50.0	usec
DEADT	71.8	usec
INTVL	125.1	usec
TIMES	16	times
DUMMY	1	times
PD	2.9007	sec
ACQTM	4099.2769	msec
PREDL	10.00000	msec
INIWT	1000.0000	msec
RESOL	0.24	Hz
PW1	6.35	usec
OBNUC	1H	
OBFRQ	399.65	MHz
OBSET	134300.00	Hz
RGAIN	-6	
SCANS	16	times
SLVNT	CDCL3	
SPINNING	13	Hz
TEMP	26.4	C

0.0031

-0.1556
-0.1757
-0.1965
-0.2080
-0.2166
-0.2294
-0.2508
-0.2599
-0.2807
-0.3008
-0.3209

0.47

0.18

0.00

-0.5 ppm
-0.4
-0.3
-0.2
-0.1
0.0
0.1

85

TEAL-I-1H

Date : Fri Jun 7 16:12:20 2002

FileName   : TEAL-I-1H.nmdata
Comment   : TEAL-I-1H
SliceHistory :
EXMODE   : non

POINT   :   32768 points
SAMPO   :   32768 points
FREQU   :   7993.6 Hz
FILTR   :   4000 Hz
DELAY   :   50.0 usec
DEADT   :   71.8 usec
INTVL   :   125.1 usec
TIMES   :   16 times
DUMMY   :   1 times
PD   :   2.9007 sec
ACQTM   : 4099.2769 msec
PREDL   : 10.00000 msec
INIWT   : 1000.0000 msec
RESOL   :   0.24 Hz
PW1   :   6.35 usec
OBNUC   : 1H
OBFRQ   :   399.65 MHz
OBSET   : 134300.00 Hz
RGAIN   :   6

SCANS   :   16 times

SLVNT   : CDCL3
SPINNING   :   13 Hz
TEMP   :   26.4 C

3.7393
3.7570
3.7747
3.7924

1.68

86

4.0   3.8   3.6   3.4   3.2   ppm

TEAL-I-1H

Date : Fri Jun 7 16:12:20 2002

FileName   : TEAL-I-1H.nmdata
Comment   : TEAL-I-1H
SliceHistory :
EXMODE   : non

POINT   32768 points
SAMPO   32768 points
FREQU   7993.6 Hz
FILTR   4000 Hz
DELAY   50.0 usec
DEADT   71.8 usec
INTVL   125.1 usec
TIMES   16 times
DUMMY   1 times
PD   2.9007 sec
ACQTM   4099.2769 msec
PREDL   10.00000 msec
INIWT   1000.0000 msec
RESOL   0.24 Hz
PW1   6.35 usec
OBNUC   1H
OBFRQ   399.65 MHz
OBSET   134300.00 Hz
RGAIN   6

SCANS   16 times

SLVNT   CDCL3
SPINNING 13 Hz
TEMP   26.4 C

0.8372

0.8830
0.8976
0.9178
0.9281
0.9379
0.9489
0.9574
0.9690

1.0502
1.0703

1.1936
1.2107
1.2168
1.2277
1.2345
1.2454
1.2522
1.3028
1.3052
1.3205

1.88

2.11

1.4   1.2   1.0   0.8   ppm

87

Date : Thu Jul 18 08:59:03 2002

FileName   : TEALII-1H.nmdata
Comment   : TEAL-II-1H
SliceHistory :
EXMODE   : non

POINT	32768	points
SAMPO	32768	points
FREQU	7993.6	Hz
FILTR	4000	Hz
DELAY	50.0	usec
DEADT	71.8	usec
INTVL	125.1	usec
TIMES	16	times
DUMMY	1	times
PD	2.9007	sec
ACQTM	4099.2769	msec
PREDL	10.00000	msec
INIWT	1000.0000	msec
RESOL	0.24	Hz
PW1	6.35	usec
OBNUC	1H	399.65 MHz
OBFRQ	134300.00	Hz
OBSET		
RGAIN	5	
SCANS	16	times
SLVNT	CDCL3	
SPINNING	12	Hz
TEMP	23.6	C

-0.8054
-0.1287
-0.1263
-0.1086
-0.1055
-0.0878
-0.0848
-0.0677
-0.0646
-0.0518
-0.0396
-0.0311
-0.0219
-0.0018
0.8513
0.9959
1.0166
1.0184
1.0374
1.0520
1.0563
1.0624
1.0746
1.0825
1.0947
1.1686
1.1856
1.2668
1.2875
1.3058
1.3235
1.3394
1.3486
1.3534
1.3663
1.3711
1.3797
1.3840
1.3882
1.3968
3.8095
3.8272
3.8449
3.8626
7.2400

0.00   1.90   0.02   4.23   1.00   0.00

10.0   7.5   5.0   2.5   0.0   ppm

Fig . A2.5
NMR of TEAL II
Synthesized in Lab

TEAL-II-1H

FileName	:	TEALII-1H.nmdata
Comment	:	TEAL-II-1H
SliceHistory	:	
EXMODE	:	non
POINT		32768 points
SAMPO		32768 points
FREQU		7993.6 Hz
FILTR		4000 Hz
DELAY		50.0 usec
DEADT		71.8 usec
INTVL		125.1 usec
TIMES		16 times
DUMMY		1 times
PD		2.9007 sec
ACQTM		4099.2769 msec
PREDL		10.00000 msec
INIWT		1000.0000 msec
RESOL		0.24 Hz
PW1		6.35 usec
OBNUC		1H
OBFRQ		399.65 MHz
OBSET		134300.00 Hz
RGAIN		-5
SCANS		16 times
SLVNT		CDCL3
SPINNING		12 Hz
TEMP		23.6 C

1.0837
1.1045
1.1063
1.1252
1.1398
1.1441
1.1502
1.1624
1.1704
1.3546
1.3754
1.3937
1.4114
1.4590

688.65

381.52

257.95

3.8973
3.9150
3.9327
3.9504

89

TEAL-III-1H

Date : Mon Aug 12 14:34:34 2002

FileName   : TEALIII-1H.nmdata
Comment   : TEAL-III-1H
SliceHistory
EXMODE   : non

POINT   32768 points
SAMPO   32768 points
FREQU   14005.6 Hz
FILTR   7000 Hz
DELAY   28.6 usec
DEADT   39.7 usec
INTVL   71.4 usec
TIMES   16 times
DUMMY   1 times
PD   4.6604 sec
ACQTM   2339.6353 msec
PREDL   10.00000 msec
INIWT   1000.0000 msec
RESOL   0.43 Hz
PW1   6.35 usec
OBNUC   1H
OBFRQ   399.65 MHz
OBSET   134300.00 Hz
RGAIN   4

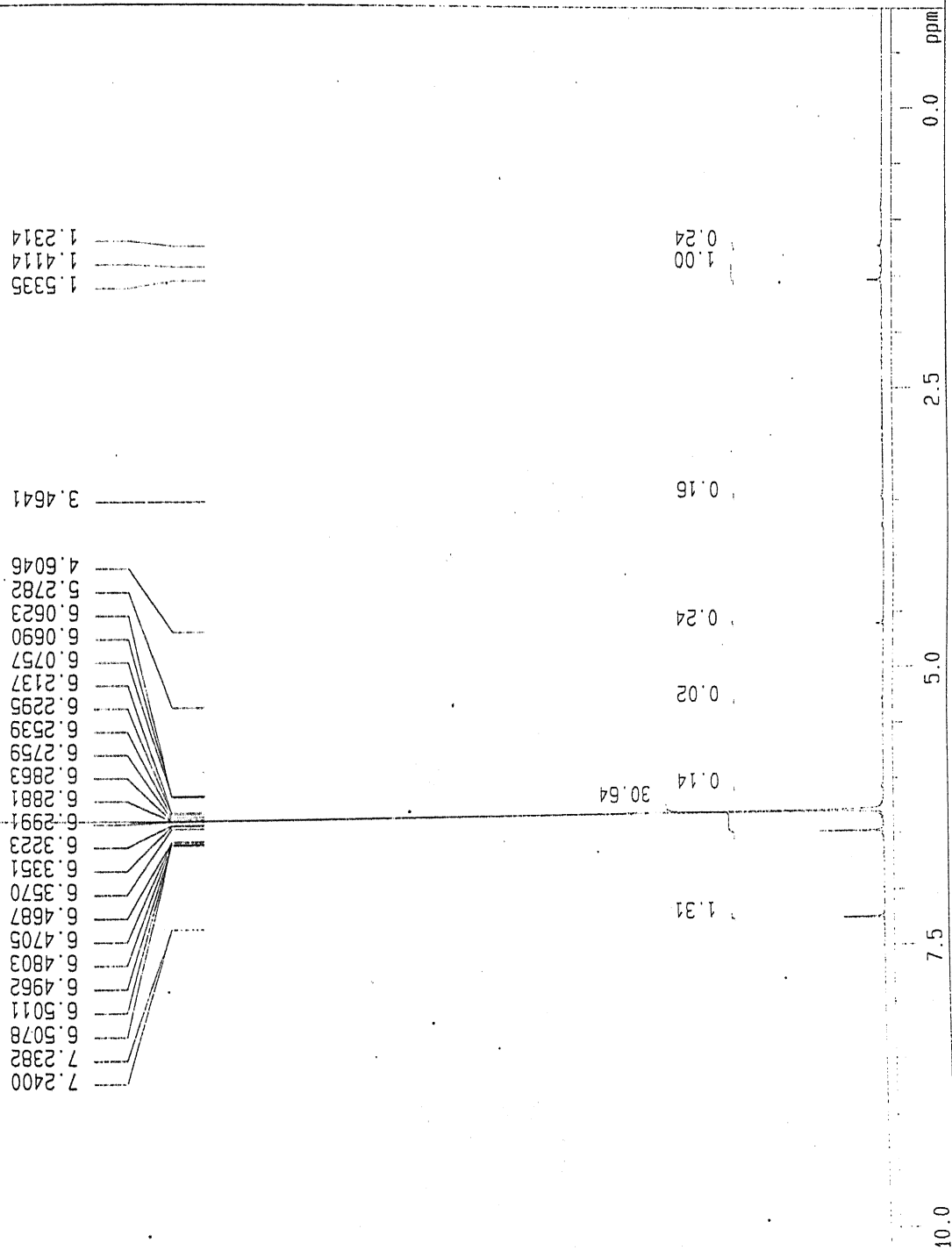SCANS   16 times

SLVNT   CDCL3
SPINNING   12 Hz
TEMP   24.7 C

Fig . A2.6
1H NMR of TEAL III
Synthesized in Lab

90

7.467

4.197
4.179
4.162
4.144

1.542
1.524
1.505
1.348
1.217
1.195
1.175
1.057
1.039
0.106
0.086
0.020
0.000
-0.021
-0.042

1.41
1.73
1.23
1.00

ppm

10.0   7.5   5.0   2.5   0.0

TEAL-III-1H

FileName   : TEALIII-1H.nmdata
Comment   : TEAL-III-1H
SliceHistory :
EXMODE   : non

POINT   32768 points
SAMPO   32768 points
FREQU   14005.6 Hz
FILTR   7000 Hz
DELAY   28.6 usec
DEADT   39.7 usec
INTVL   71.4 usec
TIMES   16 times
DUMMY   1 times
PD   4.6604 sec
ACQTM   2339.6353 msec
PREDL   10.00000 msec
INIWT   1000.0000 msec
RESOL   0.43 Hz
PW1   6.35 usec
OBNUC   1H
OBFRQ   399.65 MHz
OBSET   134300.00 Hz
RGAIN   4

SCANS   16 times
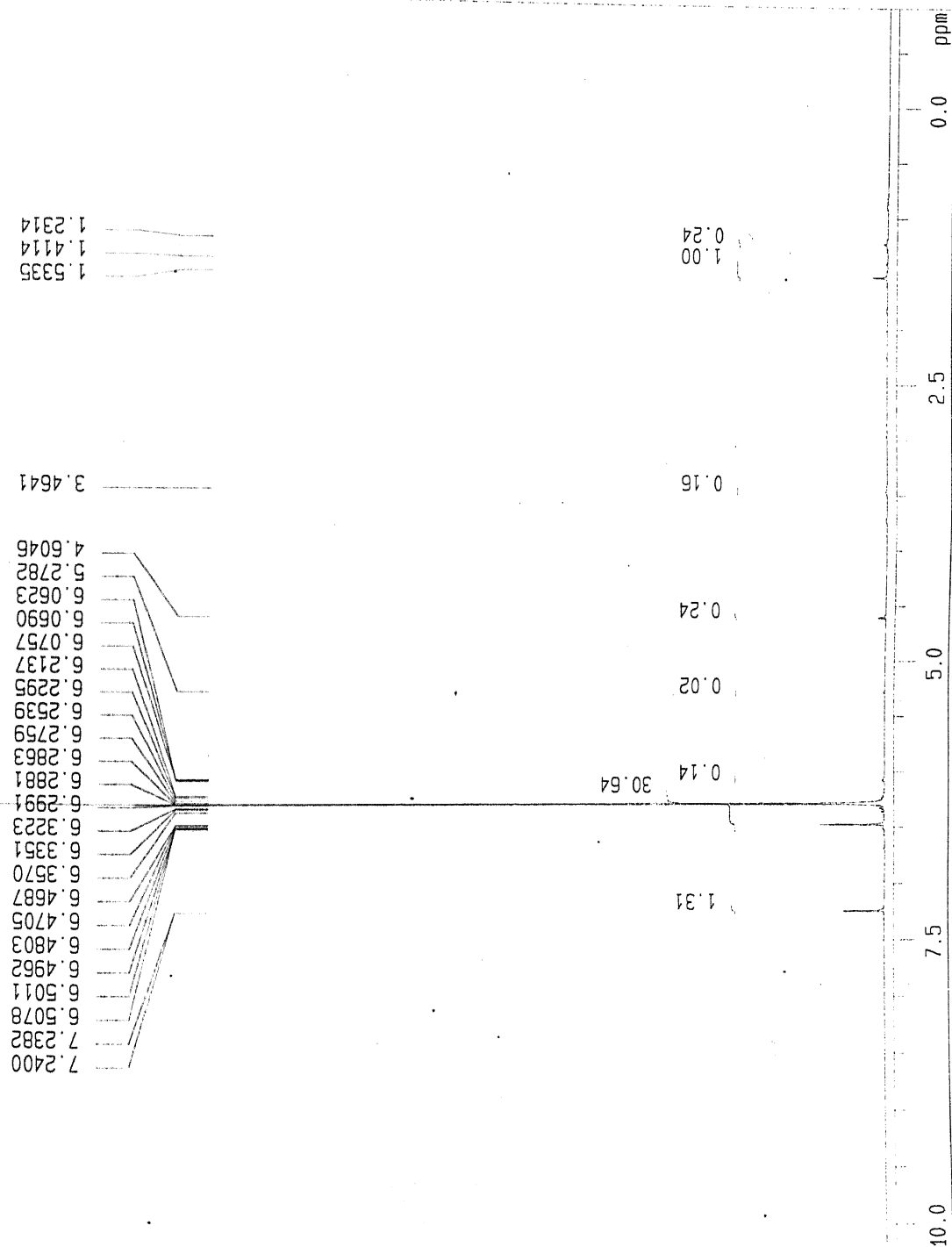
SLVNT   CDCL3
SPINNING   12 Hz
TEMP   24.7 C

-0.042
-0.021
0.000
0.020

1.175
1.195
1.217

1.505
1.524
1.542

4.144
4.162
4.179
4.197

1.41

1.73

1.23

1.00

91

ppm 0 1 2 3 4

TEAL-IV-1H

1.0605

2.08

1.1783
1.1990
1.2192

1.44

1.5115
1.5292
1.5468

1.6   1.4   1.2   1.0   0.8   ppm

93

TEAL-IV-1H

Date : Mon Aug 26 15:58:17 2002

FileName   : TEALIV-1H.nmdata
Comment   : TEAL-IV-1H
SliceHistory :
EXMODE   : non

POINT   : 32768 points
SAMPO   : 32768 points
FREQU   : 7993.6 Hz
FILTR   : 4000 Hz
DELAY   : 50.0 usec
DEADT   : 71.8 usec
INTVL   : 125.1 usec
TIMES   : 16 times
DUMMY   : 1 times
PD   : 2.9007 sec
ACQTM   : 4099.2769 msec
PREDL   : 10.00000 msec
INIWT   : 1000.0000 msec
RESOL   : 0.24 Hz
PW1   : 6.35 usec
OBNUC   : 1H
OBFRQ   : 399.65 MHz
OBSET   : 134300.00 Hz
RGAIN   : -8

SCANS   : 16 times

SLVNT   : CDCL3
SPINNING   : 13 Hz
TEMP   : 24.0 C

-0.0409
-0.0201
0.0000
0.0201

1.41

94

0.75   0.50   0.25   0.00   -0.25   -0.50   ppm

TEAL-IV-1H

Date : Mon Aug 26 15:58:17 2002

FileName   : TEALIV-1H.nmdata
Comment   : TEAL-IV-1H
SliceHistory :
EXMODE   : non

POINT   . . . . . 32768 points
SAMPO   32768 points
FREQU   7993.6 Hz
FILTR   4000 Hz
DELAY   50.0 usec
DEADT   71.8 usec
INTVL   125.1 usec
TIMES   16 times
DUMMY   1 times
PD   2.9007 sec
ACQTM   4099.2769 msec
PREDL   10.00000 msec
INIWT   1000.0000 msec
RESOL   0.24 Hz
PW1   6.35 usec
OBNUC   1H
OBFRQ   399.65 MHz
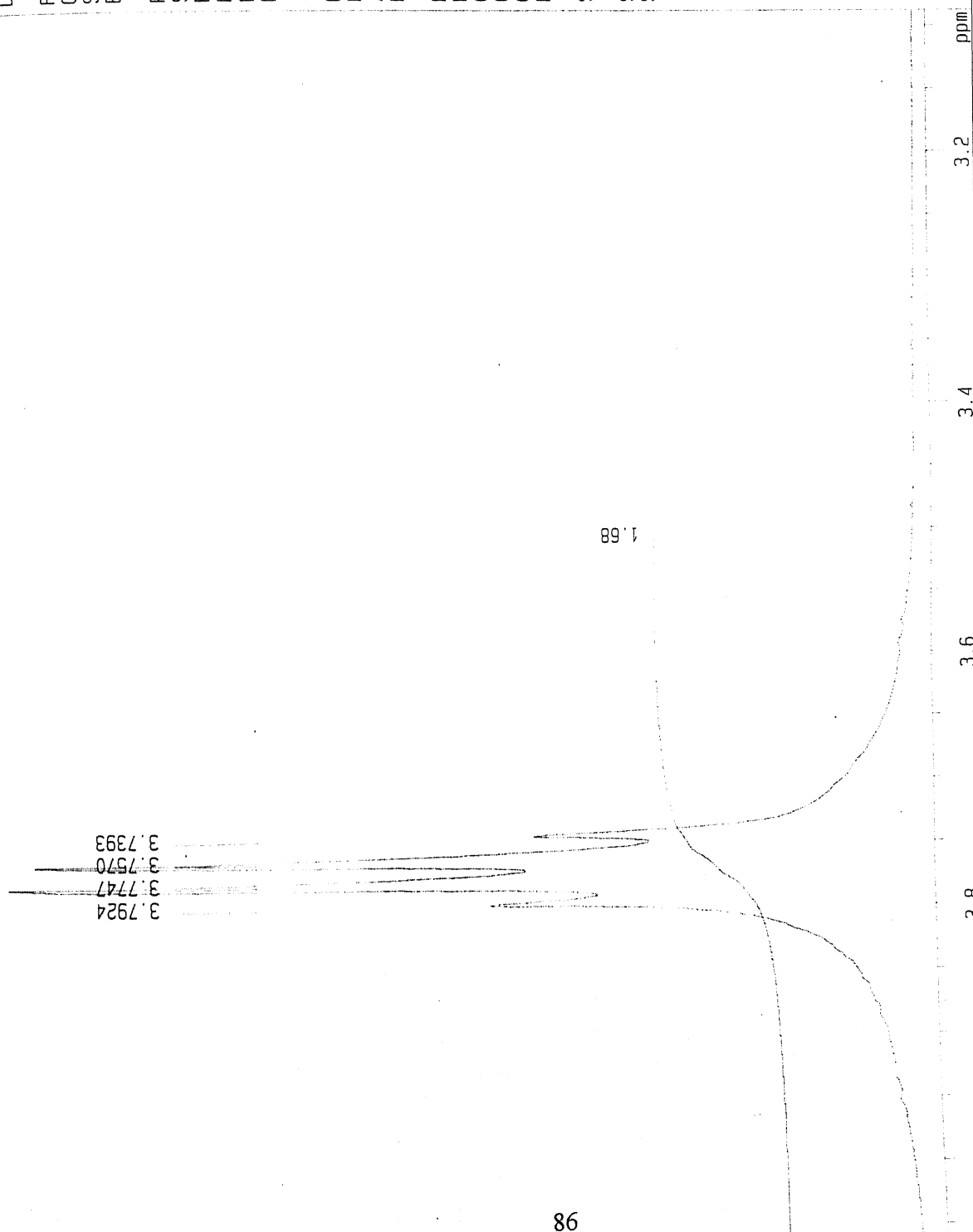OBSET   134300.00 Hz
RGAIN   8

SCANS   .   16 times

SLVNT   CDCL3
SPINNING   13 Hz
TEMP   24.0 C

95

4.2061
4.1890
4.1713
4.1530

1.00

4.75   4.50   4.25   4.00   3.75   3.50 ppm

Date : Thu Sep 5 15:01:17 2002

FileName   : TEALV-H.nmdata
Comment   : TEAL-V-1H
SliceHistory
EXMODE   : non

POINT   32768 points
SAMPO   32768 points
FREQU   7993.6 Hz
FILTR   4000 Hz
DELAY   50.0 usec
DEADT   71.8 usec
INTVL   125.1 usec
TIMES   16 times
DUMMY   0 times
PD   2.9007 sec
ACQTM   4099.2769 msec
PREDL   10.00000 msec
INIWT   0.5000 msec
RESOL   0.24 Hz
PW1   6.35 usec
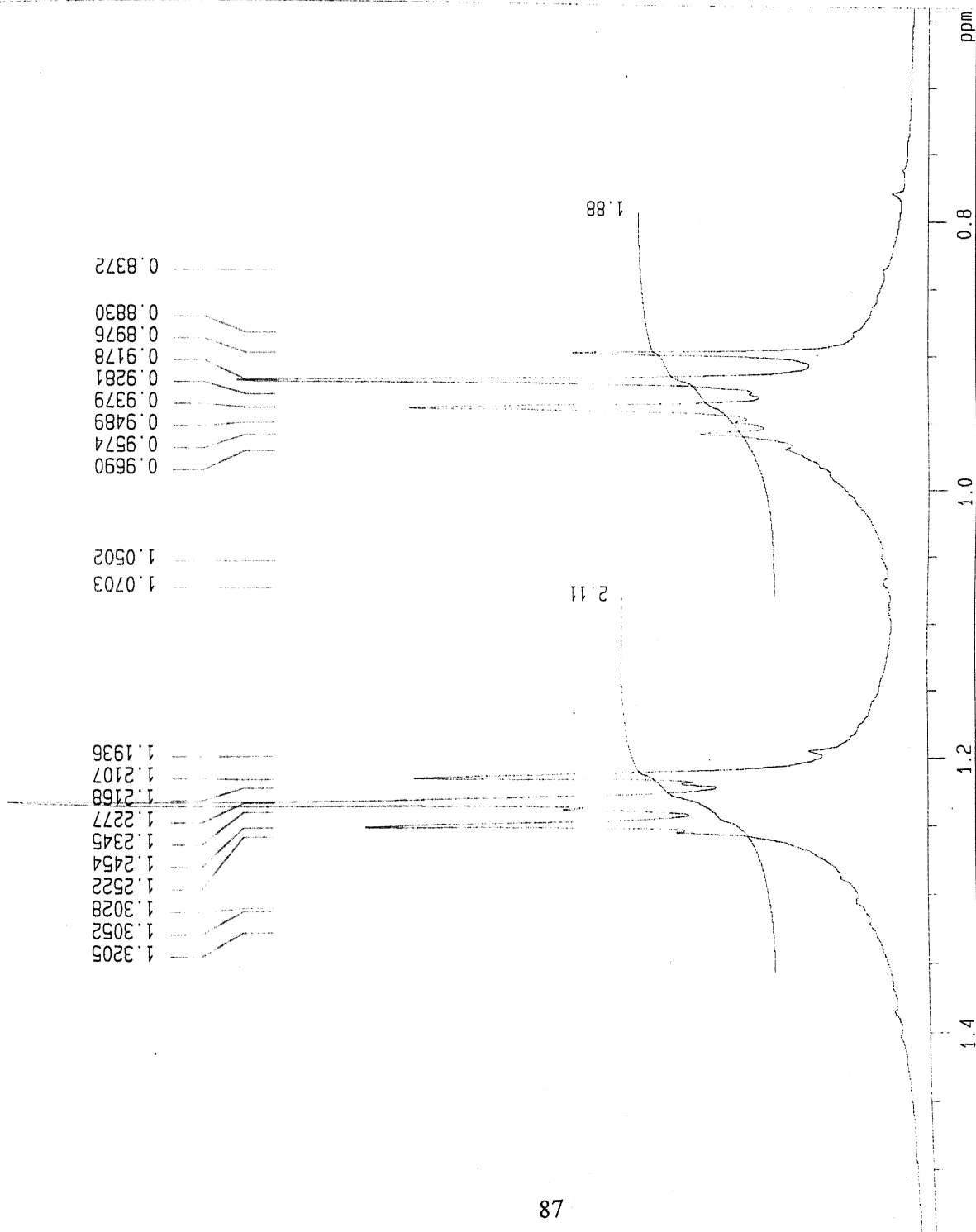OBNUC   1H
OBFRQ   399.65 MHz
OBSET   13300.00 Hz
RGAIN   4

SCANS   16 times

SLVNT   CDCL3
SPINNING   13 Hz
TEMP   25.2 C

-0.0555
-0.0409
-0.0354
-0.0207
0.0000
0.0201
0.0836
0.1037
1.0587
1.1423
1.1624
1.1771
1.1978
1.2180
1.2363
1.4718
1.4901
1.4938
1.5066
1.5108
1.5249
1.5426
4.0340
4.0517
4.1249
4.1420
4.1597
4.1774
4.1951

1.43
2.06
1.49
1.00

0 ppm
2
4
6
8
10

Fig. A2.8
1H NMR of TEAL V
Synthesized in Lab

96

TEAL-V-1H

1.0587

1.1771
1.1978
1.2180

1.5066
1.5249
1.5426

0.02

1.98

1.49

1.0ppm   1.2   1.4   1.6

98

TEAL-V-1H

Date : Thu Sep 5 15:01:17 2002

FileName   : TEALV-H.nmdata
Comment   : TEAL-V-1H
SliceHistory :
EXMODE   : non

POINT   32768 points
SAMPO   32768 points
FREQU   7993.6 Hz
FILTR   4000 Hz
DELAY   50.0 usec
DEADT   71.8 usec
INTVL   125.1 usec
TIMES   16 times
DUMMY   0 times
PD   2.9007 sec
ACQTM   4099.2769 msec
PREDL   10.00000 msec
INIWT   0.5000 msec
RESOL   0.24 Hz
PW1   6.35 usec
OBNUC   1H
OBFRQ   399.65 MHz
OBSET   134300.00 Hz
RGAIN   4

SCANS   16 times
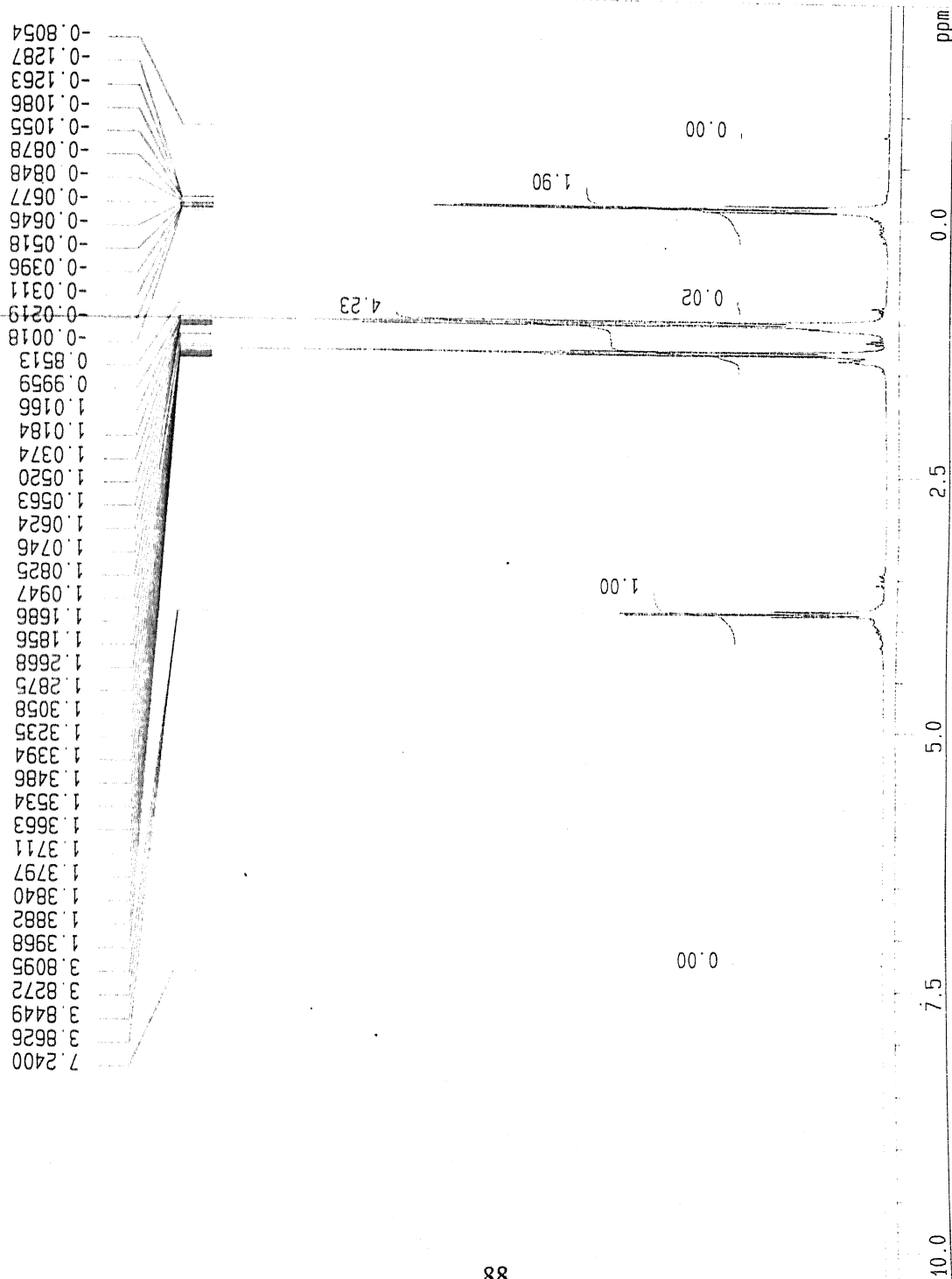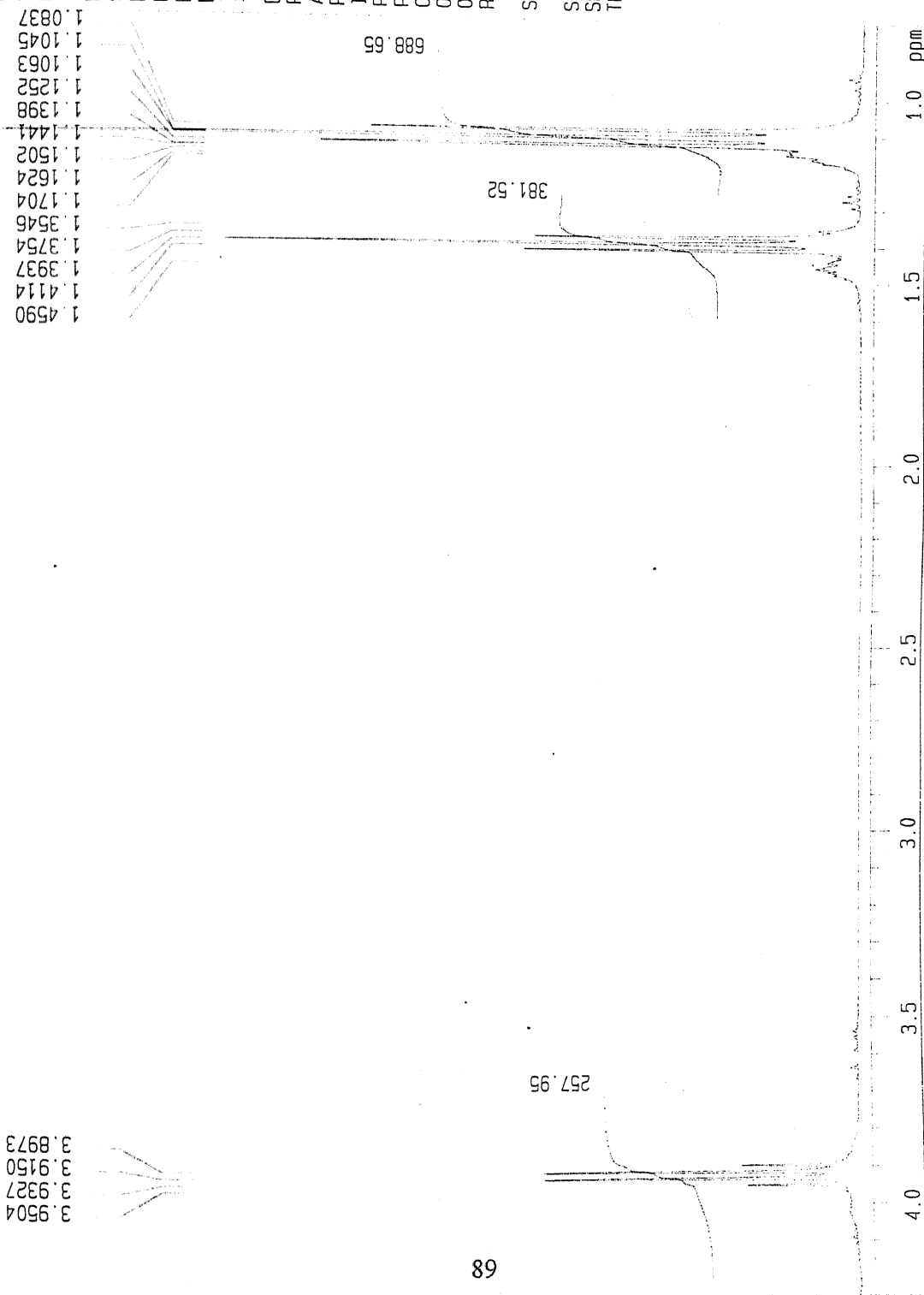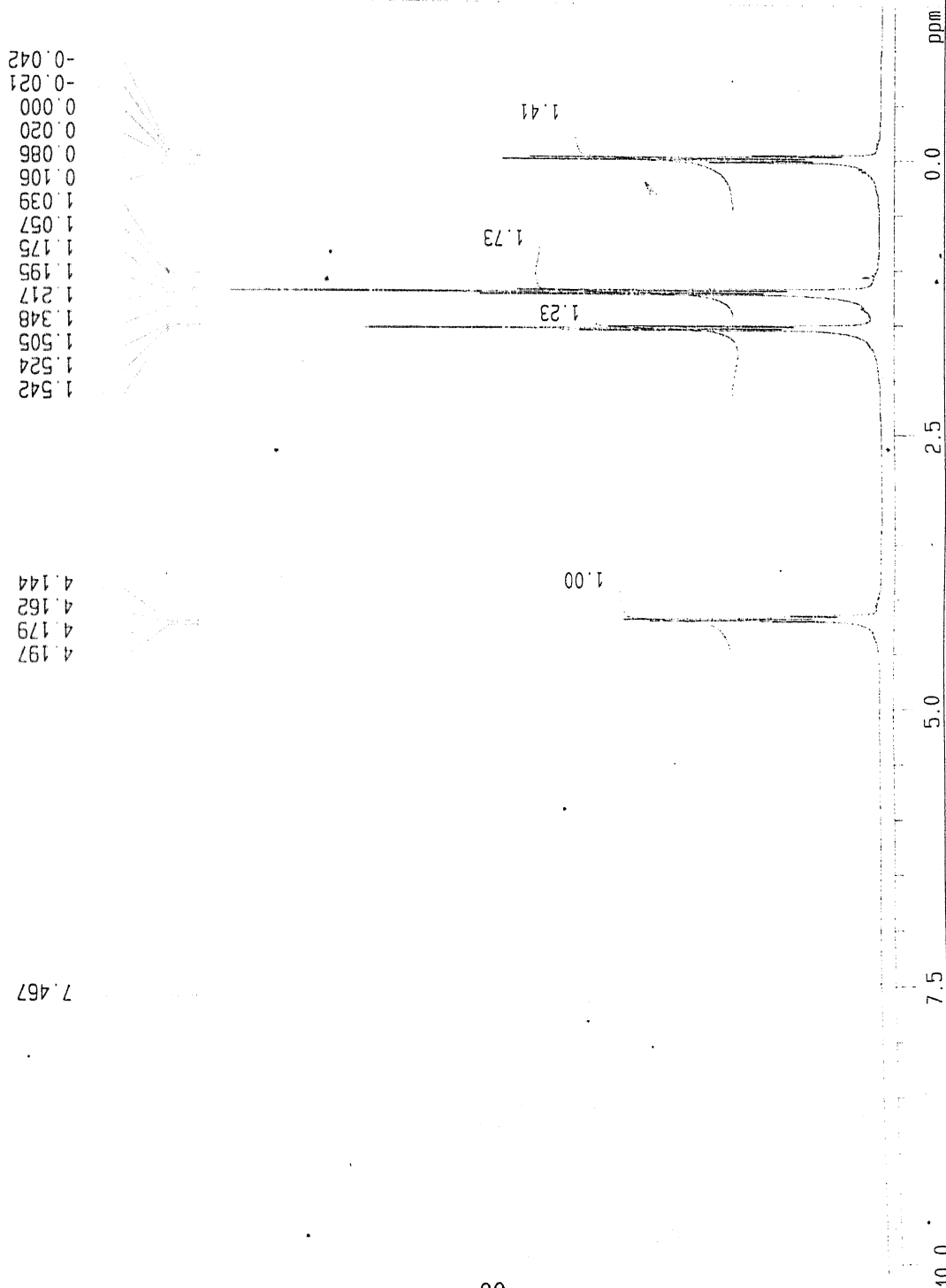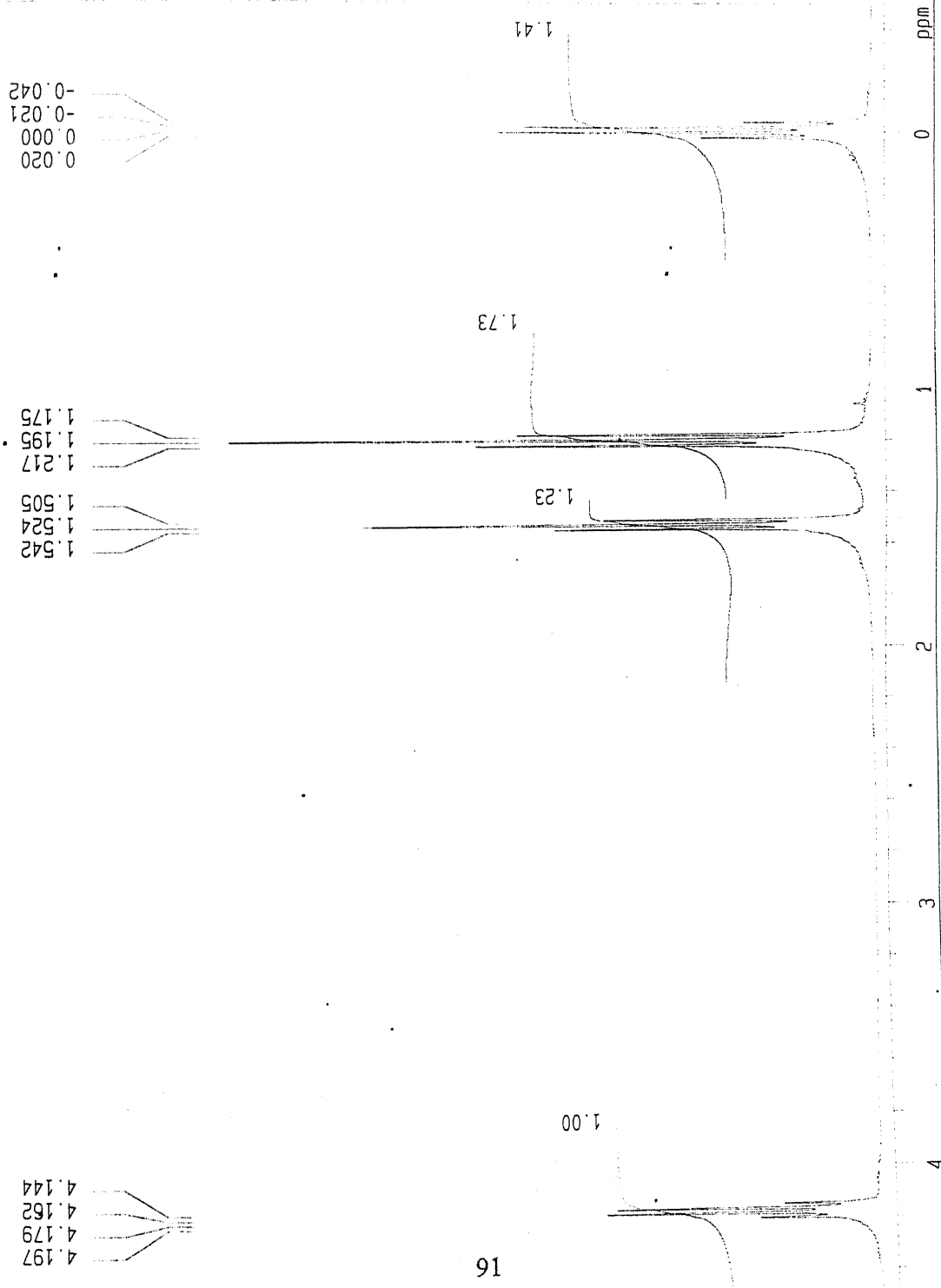
SLVNT   : CDCL3
SPINNING   : 13 Hz
TEMP   : 25.2 C

-0.0409
-0.0207
0.0000
0.0201
0.0635
0.0836
0.1037
0.1257

1.13
0.07

0.15   0.10   0.05   0.00   -0.05   -0.10   ppm

Date : Tue Sep 17 08:40:21 2002

FileName	: TEALII-13C.nmdata
Comment	: TEAL-II-13C
SliceHistory	:
EXMODE	: bcm

POINT	32768	points
SAMPO	32768	points
FREQU	27100.3	Hz
FILTR	13550	Hz
DELAY	14.8	usec
DEADT	19.6	usec
INTVL	36.9	usec
TIMES	300	times
DUMMY	1	times
PD	1.7909	sec
ACQTM	1209.1393	msec
PREDL	10.00000	msec
INIWT	1000.0000	msec
RESOL	0.83	Hz
PW1	5.15	usec
OBNUC	13C	
OBFRQ	100.40	MHz
OBSET	135500.00	Hz
RGAIN	26	
IRNUC	1H	
IRFRQ	399.65	MHz
IRSET	134300.00	Hz
IRRPW	47.0	usec
IRRNS	0	
SCANS	137	times
SLVNT	CDCL3	
SPINNING	13	Hz
TEMP	21.5	C
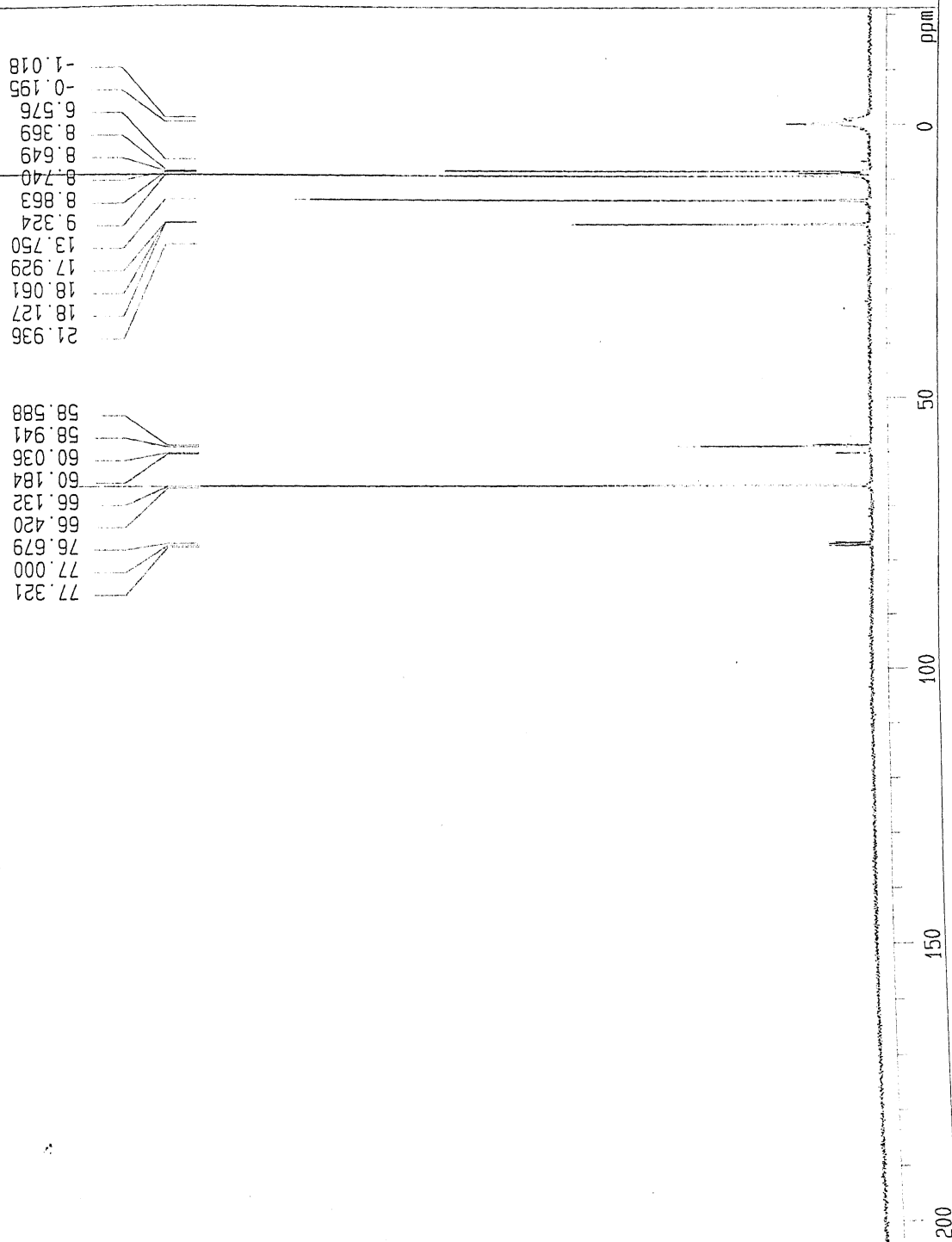
Fig. A2.9
13C NMR of TEAL II
Synthesized in Lab

Peak labels:
-1.018
-0.195
6.576
8.369
8.649
8.740
8.863
9.324
13.750
17.929
18.061
18.127
21.936

58.588
58.941
60.036
60.184
66.132
66.420
76.679
77.000
77.321

ppm axis: 0   50   100   150   200

100

Date : Tue Aug 13 13:58:50 2002

FileName : TEALIII-C.nmdata
Comment : TEAL-III-13C
EXMODE : bcm

POINT : 32768 points
SAMPO : 32768 points
FREQU : 27100.3 Hz
FILTR : 13550 Hz
DELAY : 14.8 usec
DEADT : 19.5 usec
INTVL : 36.9 usec
TIMES : 300 times
DUMMY : 1 times
PD : 1.7909 sec
ACQTM : 1209.1393 msec
PREDL : 10.00000 msec
INIWT : 10.0000 msec
RESOL : 0.83 Hz
PW1 : 5.20 usec
OBNUC : 13C
OBFRQ : 100.40 MHz
OBSET : 135500.00 Hz
RGAIN : 25
IRNUC : 1H
IRFRQ : 399.65 MHz
IRSET : 134300.00 Hz
IRRPW : 50.0 usec
IRRNS : 0

SCANS : 300 times

SLVNT : CDCL3
SPINNING : 13 Hz
TEMP : 26.0 C

Peaks:
0.000
8.548
9.519
13.731
18.305
58.807
59.153
66.459
76.907
77.228
77.541

200   150   100   50   0 ppm

Fig . A2.10
13C NMR of TEAL III
Synthesized in Lab

101

TEAL-IV-13C

Date : Mon Aug 26 15:54:52 2002

FileName	: TEALIV-13C.nmdata
Comment	: TEAL-IV-13C
SliceHistory	:
EXMODE	: bcm
POINT	32768 points
SAMPO	32768 points
FREQU	27100.3 Hz
FILTR	13550 Hz
DELAY	14.8 usec
DEADT	19.5 usec
INTVL	36.9 usec
TIMES	300 times
DUMMY	3 times
PD	1.7909 sec
ACQTM	1209.1393 msec
PREDL	10.00000 msec
INIWT	1000.0000 msec
RESOL	0.83 Hz
PW1	5.20 usec
OBNUC	13C
OBFRQ	100.40 MHz
OBSET	135500.00 Hz
RGAIN	.26
IRNUC	1H
IRFRQ	399.65 MHz
IRSET	134419.00 Hz
IRRPW	60.0 usec
IRRNS	0
SCANS	56 times
SLVNT	CDCL3
SPINNING	12 Hz
TEMP	24.1 C
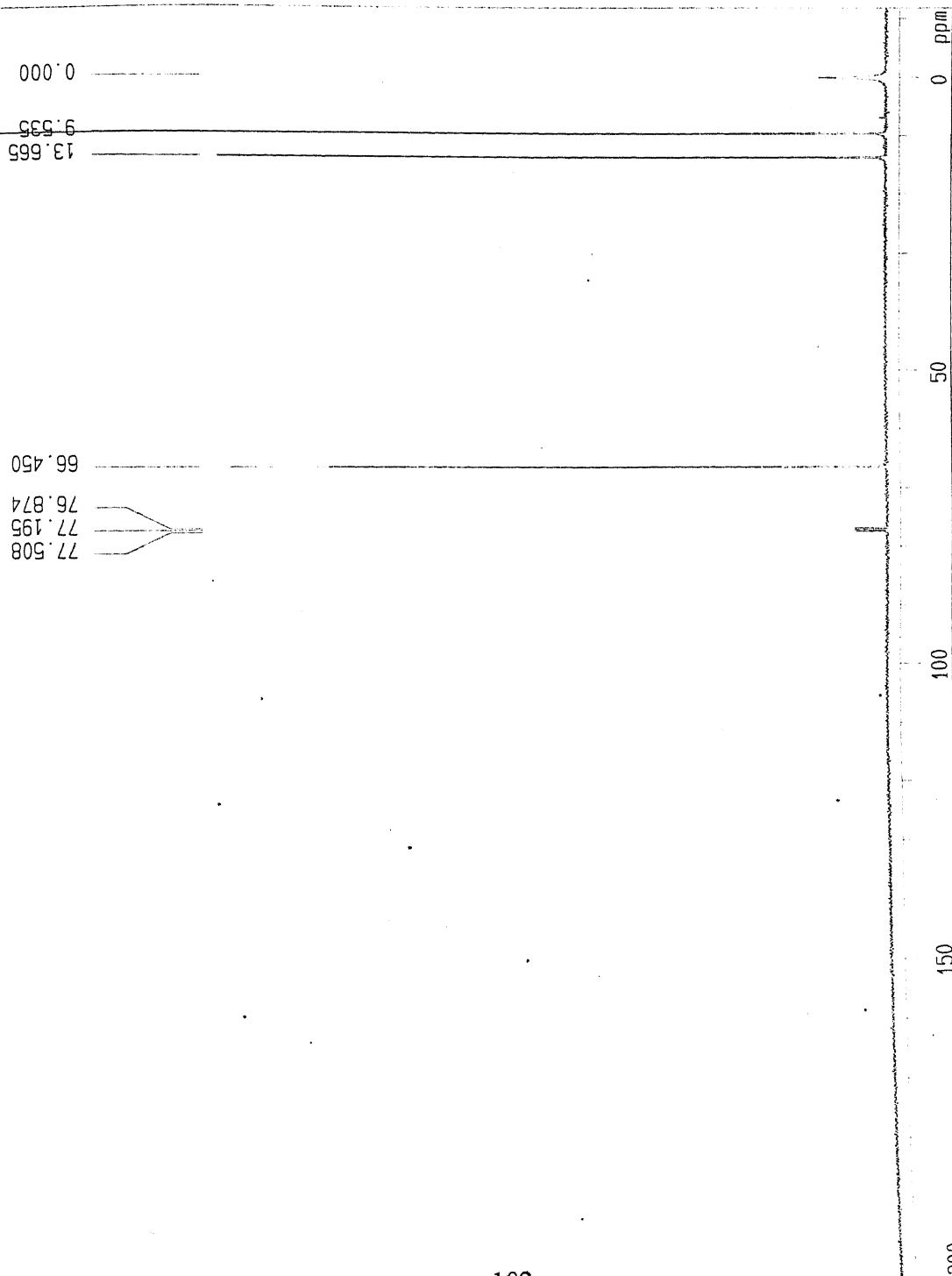
Fig. A2.11
13C NMR of TEAL IV
Synthesized in Lab

102

EAO-II-1H

Date : Mon Sep 16 15:49:59 2002

FileName	:	EAOII-1H.nmdata
Comment	:	EAO-II-1H
SliceHistory	:	
EXMODE	:	non
POINT		32768 points
SAMPO		32768 points
FREQU		7993.6 Hz
FILTR		4000 Hz
DELAY		50.0 usec
DEADT		72.4 usec
INTVL		125.1 usec
TIMES		16 times
DUMMY		1 times
PD		2.9007 sec
ACQTM		4099.2769 msec
PREDL		10.00000 msec
INIWT		1000.0000 msec
RESOL		0.24 Hz
PW1		5.25 usec
OBNUC		1H
OBFRQ		399.65 MHz
OBSET		134300.00 Hz
RGAIN		19
SCANS		16 times
SLVNT		CDCL3
SPINNING		12 Hz
TEMP		22.9 C

Fig. A2.12
1H NMR of EAO II
Synthesized in Lab

Peak labels:
7.0685
7.0874
7.0935
7.1069
7.1124
7.1667
7.1814
7.2003
7.2040

2.2840
1.4761
1.1722
0.0000

Integration values:
1.02
0.05
2.00
9.50
48.18
1.00
80.73

ppm axis: 0.0 2.5 5.0 7.5 10.0

103a
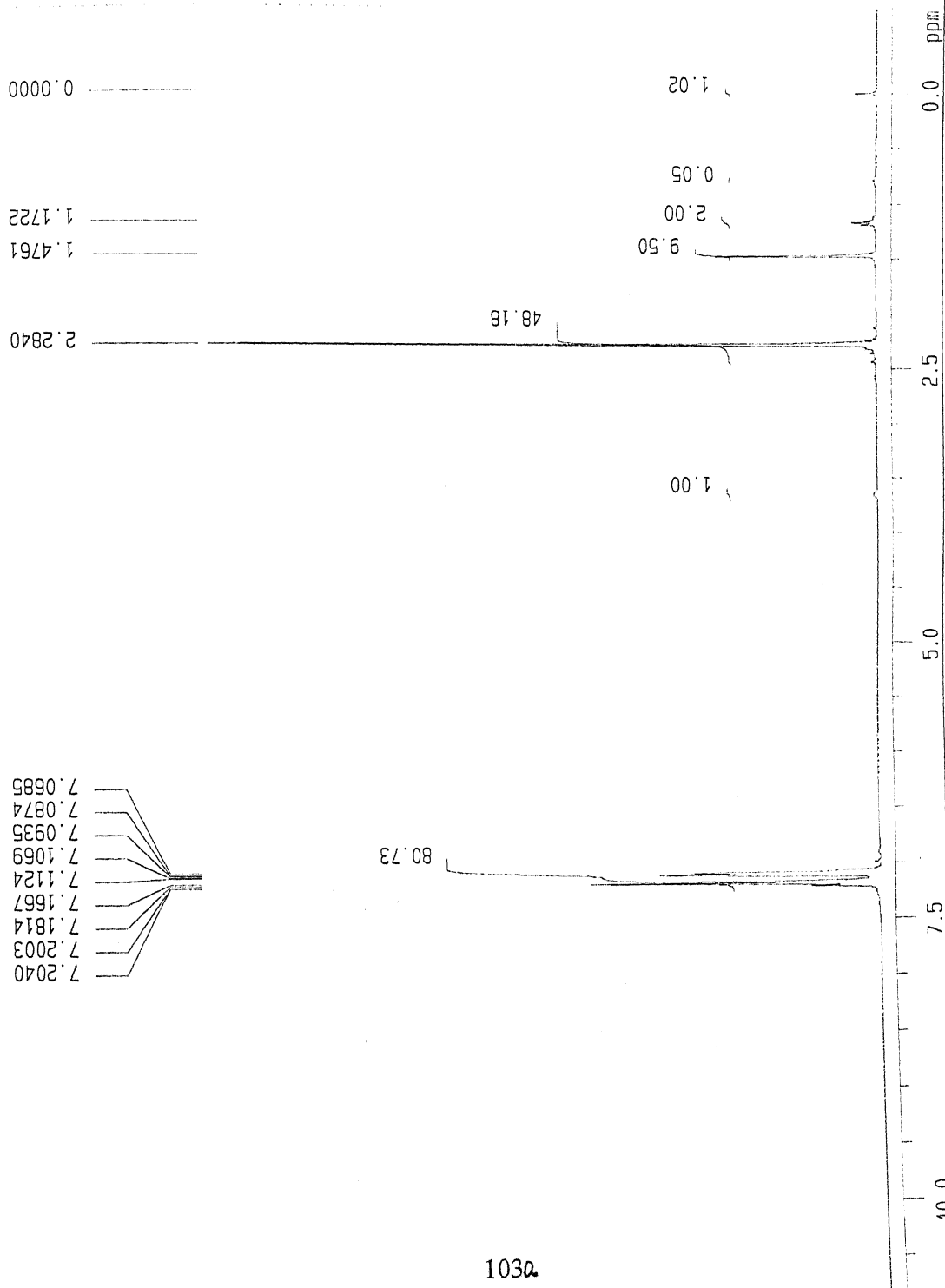
Appendix 3
Experimental Calculation

Table A3.1
Calculation for synthesis of Cp$_2$TiCl$_2$

Basis: Cp = 15 gms

Reactant	Weight (gm)	Moles	Volume (ml)	Equivalent
Cp	15	0.2269	----	1
Na	5.741	0.2496	----	1.1
TiCl$_4$	21.5203	0.11345	12.439	0.5

Table A3.2
Calculation for Synthesis of TEAL

Reactant	F. Wt	Density(gm/ml)	Weight(gm)	Volume(ml)	mole	Equivalent
AlCl3	133.34	2.44	33.335	----	0.25	1
C2H5Br	108.97	1.46	----	74.63	1	4
Mg	24.31	----	36.465	----	1.5	6

Table A3.3
Calculation for Synthesis of Ethyl aluminoxane from Al$_2$(SO$_4$)$_3$.16H$_2$O

Reactant	Volume(ml)	Weight (gm)	Mole	Equivalent
TEAL	13.67	----	0.1	8
Al$_2$(SO$_4$)$_3$.16H$_2$O	----	7.398	0.012	1

Table A3.4
Sample Calculation for Synthesis of Methyl Aluminoxane using Al$_2$(SO$_4$)$_3$.14H$_2$O as Source of Water (U.S. 1991000686599)

37 gm Al$_2$SO$_4$.14H$_2$O (As) $\equiv$ 500m mole (CH$_3$)$_3$Al (TMA)

Hence moles of As = 0.06228

$$\frac{\text{Moles of TMA}}{\text{Moles of As}} = \frac{0.5}{0.062} \approx 8 \text{ mole}$$

Table A 3.5
Calculation for Synthesis of Ethyl aluminoxane from Etheral Water

TEAL $\equiv$ 26 ml $\equiv$ 21.71 gms $\equiv$ 0.19 mole
H$_2$O $\equiv$ 3.422 ml $\equiv$ 3.422 gms $\equiv$ 0.19 mole

TEAL / H$_2$O = 1/1(mole ratio)

Appendix 4
CHN Analysis

Eager 200 Report

Page: 1   Sample: PV-GAIL (PVGAIL)

S/W version	: 1.04	Company Name	: IIT
Operator ID	:	Method File	: TEST0111.MTH
Method Name	: test2606	Printed	: 9/24/2002 13:27
Analysed	: 09-24-02 05:08		

Sample ID	: PV-GAIL (# 38)	Channel	: E.A. Channel A
Analysis Type	: UnkNown (Area)	Sample weight	: 1.996
Chromatogram	: C:\OLDDAT~1\ABC\PVGAIL.DAT		

Calib. method : using 'Least Squares to Linear fit'

!!! Warning missing one or more peaks.

Warning Chromatogram has been subjected to manual integration.

Element Name	Element %	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	-1.0984290E+00	68	58839	mi	145.122100	
Carbon	84.5695	85	8538900	mi	1.000000	
Hydrogen	13.5571	258	3849860	mi	2.217977	

Table A 4.1 C H N Analysis (PV GAIL)

Eager 200 Report

Page: 1   Sample: PV (PV)

S/W version	:	1.04	Company Name	: IIT
Operator ID	:		Method File	: TEST0111.MTH
Method Name	:	test2606	Printed	: 9/24/2002 01:50
Analysed	:	09-18-02 19:41		

Sample ID	:	PV (# 11)	Channel	: E.A. Channel A
Analysis Type	:	UnKnown (Area)	Sample weight	: 1.63
Chromatogram	:	C:\OLDDAT~1\ABC\PV.DAT		

Calib. method : using 'Least Squares to Linear fit'

!!! Warning missing one or more peaks.

Warning Chromatogram has been subjected to manual integration.

Element Name	Element %	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	-7.4997807E-01	77	83031 mi		76.933430	
Carbon	77.1249	86	6387826 FU		1.000000	
Hydrogen	12.4294	252	2721482 RS		2.347187	

Table A 4.2 C H N Analysis (PV IV)

Eager 200 Report

Page: 1   Sample: PV-6 (PV6)

S/W version	:	1.04	Company Name	:	IIT
Operator ID	:		Method File	:	TEST0111.MTH
Method Name	:	test2606	Printed	:	9/24/2002 20:12
Analysed	:	09-24-02 04:26			

Sample ID	:	PV-6 (# 34)	Channel	:	E.A. Channel A
Analysis Type	:	UnkNown (Area)	Sample weight	:	1.72
Chromatogram	:	C:\OLDDAT~1\ABC\PV6.DAT			

Calib. method : using 'Least Squares to Linear fit'

!!! Warning missing one or more peaks.

Element Name	Element %	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	0.3015	77	126449	FU	48.136380	
Carbon	69.5836	86	6086791	TL	1.000000	
Hydrogen	10.7966	232	2441094	CR	2.493468	

Table A 4.3 C H N Analysis (PV VI)

Eager 200 Report

Page: 1   Sample: PV-9 (PV9)

S/W version	: 1.04	Company Name	: IIT
Operator ID	:	Method File	: TEST0111.MTH
Method Name	: test2606	Printed	: 9/24/2002 07:05
Analysed	: 09-24-02 04:36		

Sample ID	: PV-9 (# 35)	Channel	: E.A. Channel A
Analysis Type	: UnkNown (Area)	Sample weight	: 1.688
Chromatogram	: C:\OLDDAT~1\ABC\PV9.DAT		

Calib. method : using 'Least Squares to Linear fit'

!!! Warning missing one or more peaks.

Warning Chromatogram has been subjected to manual integration.

Element Name	Element %	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	-1.5971026E+00	76	46284	mi	152.832200	
Carbon	82.6133	86	7073666	mi	1.000000	
Hydrogen	13.1366	242	3039200	CR	2.327476	

Table A 4.4 C H N Analysis (PV IX)

Eager 200 Report

Page: 1   Sample: PV-10 (PV10)

S/W version	: 1.04	Company Name	: IIT
Operator ID	:	Method File	: TEST0111.MTH
Method Name	: test2606	Printed	: 9/24/2002 07:06
Analysed	: 09-24-02 04:48		

Sample ID	: PV-10 (# 36)	Channel	: E.A. Channel A
Analysis Type	: UnkNown (Area)	Sample weight	: 1.714
Chromatogram	: C:\OLDDAT~1\ABC\PV10.DAT		

Calib. method : using 'Least Squares to Linear fit'

!!! Warning missing one or more peaks.

Warning Chromatogram has been subjected to manual integration.

Element Name	Element %	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	-2.1395690E+00	77	22060	mi	318.793000	
Carbon	80.8801	86	7032584	mi	1.000000	
Hydrogen	13.2174	244	3118831	mi	2.254878	

Table A 4.5 C H N Analysis (PV X)

Eager 200 Report

Page: 1   Sample: PV-11 (PV11)

S/W version	:	1.04
Operator ID	:	
Method Name	:	test2606
Analysed	:	09-24-02 04:58

Company Name	:	IIT
Method File	:	TEST0111.MTH
Printed	:	9/24/2002 07:07

Sample ID	:	PV-11 (# 37)
Analysis Type	:	UnkNown (Area)
Chromatogram	:	C:\OLDDAT~1\ABC\PV11.DAT

Channel	:	E.A. Channel A
Sample weight	:	1.814

Calib. method : using 'Least Squares to Linear fit'

!!! Warning missing one or more peaks.

Warning Chromatogram has been subjected to manual integration.

Element Name	Element %	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	-1.0020422E+00	77	68186 mi		106.589600	
Carbon	79.0196	86	7267884 mi		1.000000	
Hydrogen	12.7994	247	3212345 mi		2.262486	

Table A 4.6 C H N Analysis (PV XI)

Eager 200 Report

Page: 1   Sample: PV-12 (PV12)

S/W version	: 1.04	Company Name	: IIT
Operator ID	:	Method File	: TESTO111.MTH
Method Name	: test2606	Printed	: 9/24/2002 13:26
Analysed	: 09-24-02 05:18		

Sample ID	: PV-12 (# 39)	Channel	: E.A. Channel A
Analysis Type	: UnkNown (Area)	Sample weight	: 1.902
Chromatogram	: C:\OLDDAT~1\ABC\PV12.DAT		

Calib. method : using 'Least Squares to Linear fit'

!!! Warning missing one or more peaks.

Warning Chromatogram has been subjected to manual integration.

Element Name	Element %	Ret.Time	BC	Area	Area ratio	K factor
Nitrogen	-1.6223413E+00	76		36563 mi	213.022800	
Carbon	80.8489	85		7788741 mi	1.000000	
Hydrogen	13.1193	252		3500226 mi	2.225211	

Table A 4.7 C H N Analysis (PV XII)

Eager 200 Report

Page: 1   Sample: PV-13 (PV13)

```
S/W version    : 1.04               Company Name : IIT
Operator ID    :                    Method File  : TEST0111.MTH
Method Name    : test2606           Printed      : 9/24/2002  07:10
Analysed       : 09-24-02  05:28

Sample ID      : PV-13 (# 40)       Channel      : E.A. Channel A
Analysis Type  : UnkNown (Area)     Sample weight : 1.828
Chromatogram   : C:\OLDDAT~1\ABC\PV13.DAT

Calib. method  : using 'Least Squares to Linear fit'

!!! Warning missing one or more peaks.
```

Element Name	Element %	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	-1.1998134E+00	68	58820	FU	114.733600	
Carbon	72.7242	86	6748589	TL	1.000000	
Hydrogen	12.0560	243	3016575	CR	2.237169	

Table A 4.8 C H N Analysis (PV XIII)

Eager 200 Report

Page: 1   Sample: PV-15 (PV15)

S/W version	: 1.04		Company Name	:	IIT
Operator ID	:		Method File	:	TEST0111.MTH
Method Name	: test2606		Printed	:	9/24/2002 13:31
Analysed	: 09-24-02 05:52				

Sample ID	: PV-15 (# 42)		Channel	:	E.A. Channel A
Analysis Type	: UnkNown (Area)		Sample weight	:	1.732
Chromatogram	: C:\OLDDAT~1\ABC\PV15.DAT				

Calib. method : using 'Least Squares to Linear fit'

!!! Warning missing one or more peaks.

Warning Chromatogram has been subjected to manual integration.

Element Name	Element %	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	-1.7336296E+00	77	38634	mi	140.797200	
Carbon	61.6164	87	5439569	mi	1.000000	
Hydrogen	10.9243	236	2499286	mi	2.176449	

Table A 4.10 C H N Analysis (PV XV)

Table A 5

I.R. spectra[1] (4000-600 cm.$^{-1}$) of $(C_5H_5)_2MX_2$ systems[a]

	Ti				Zr				Hf				Assignment
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I	
	3118sh	3118s	3110s	3104s	3125s	3108s	3107s	3103s	3130m	3113s	3110s	3108s	(C-H), in plane
	3109s				3114s				3115sh				(C-H), A in plane
	1450s	1445s	1445s	1443s	1440s	1443s	1442s	1443s	1440s	1441s	1441s	1443s	(C-C), in plane
	1370w	1375w	1375w	1373w	1365w	1368w	1366w	1368w	1370w	1367w	1365w	1367w	(C-C), A in plane
	1130vw	1131vw	1130vw	1130vw		1125vw	1125vw	1124vw		1126vw	1126vw	1125vw	Symme Breathi
	1030sh	1028m	1022sh	1022s	1022sh	1022s	1021sh	1018sh	1020sh	1023s	1022sh	1020sh	(C-H), inplane
	1015s	1014s	1015s	1013s	1013s	1013s	1012s	1013s	1013s	1013s	1013s	1012s	∂(C-H)
	874m	868m	872m	866sh	853m	851s	850s	851m	857s	854s	853s	854s	Out o deform
			864m	858m		840s	840m	837m	849sh	840s	841s	838m	
	820vs	820vs	819vs	818vs	815vs	811vs	811vs	811vs	819vs	814vs	813vs	814vs	∂(C-H)
	606w				618w				621w				Out o deform

[a] Recorded on a P.E. 337 grating spectrometer, as mulls in hexachlorobutadinene (4000-1250 cm.$^{-1}$) and nujol(1250-600 cm.$^{-1}$).

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Table A6

Characterization and Preparative Details[1] for π-$(C_5H_5)_2MX_2$

Compound π-$(C_5H_5)_2MX_2$	Colour	Melting point	Max. Reported Yield	Process Solvent	Required Percentage		
					C	H	X (Cl,Br, I,
π-$(C_5H_5)_2TiF_2$	Yellow	(Decomp.)	60	----	55.6	4.7	17.6
π-$(C_5H_5)_2TiCl_2$	Red	289 ± 2	---	T.H.F.	48.2	4.1	---
π-$(C_5H_5)_2TiBr_2$	Deepred	309	100	Benzene	35.5	2.9	47.3
π-$(C_5H_5)_2TiI_2$	Black	315 – 317	98	Acetone	27.8	2.3	58.8
π-$(C_5H_5)_2ZrF_2$	Colourless	>250	65	Ether	46.3	3.9	---
π-$(C_5H_5)_2ZrCl_2$	Colourless	242 – 245	---	T.H.F.	41.1	3.5	---
π-$(C_5H_5)_2ZrBr_2$	Colourless	259 – 260	100	Ether	31.5	2.6	42.0
π-$(C_5H_5)_2ZrI_2$	Yellow	299 – 300	100	----	25.2	2.4	53.4
π-$(C_5H_5)_2HfF_2$	Colourless	> 200	61	Water	34.6	2.9	---
π-$(C_5H_5)_2HfCl_2$	Colourless	> 300	81	T.H.F.	31.6	2.7	---
π-$(C_5H_5)_2HfBr_2$	Off-white	265 – 267	98	dichloromethane	25.6	2.1	---
π-$(C_5H_5)_2HfI_2$	Yellow	303 - 305	100	dichloromethane	21.3	1.8	45.1

T.H.F. = Tetrahydrofuran, Ether = diethylether

[1] P.M. Druce, "Metallocene Halides, Part I, Synthesis, Spectra and Redistribution Equilibria of π-$(C_5H_5)_2MX_2$" J. Chem. Soc. (A), 2106, (1969)

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Chemical shift for Cp_2TiCl_2 & Cp_2ZrCl_2

Compound	NMR value Chemical shift
Cp_2TiCl_2	6.58
Cp_2ZrCl_2	6.50

TABLE A 8
Major metal containing fragments in the mass spectra of $(\pi\text{-}C_5H_5)_2MX_2$)[1]

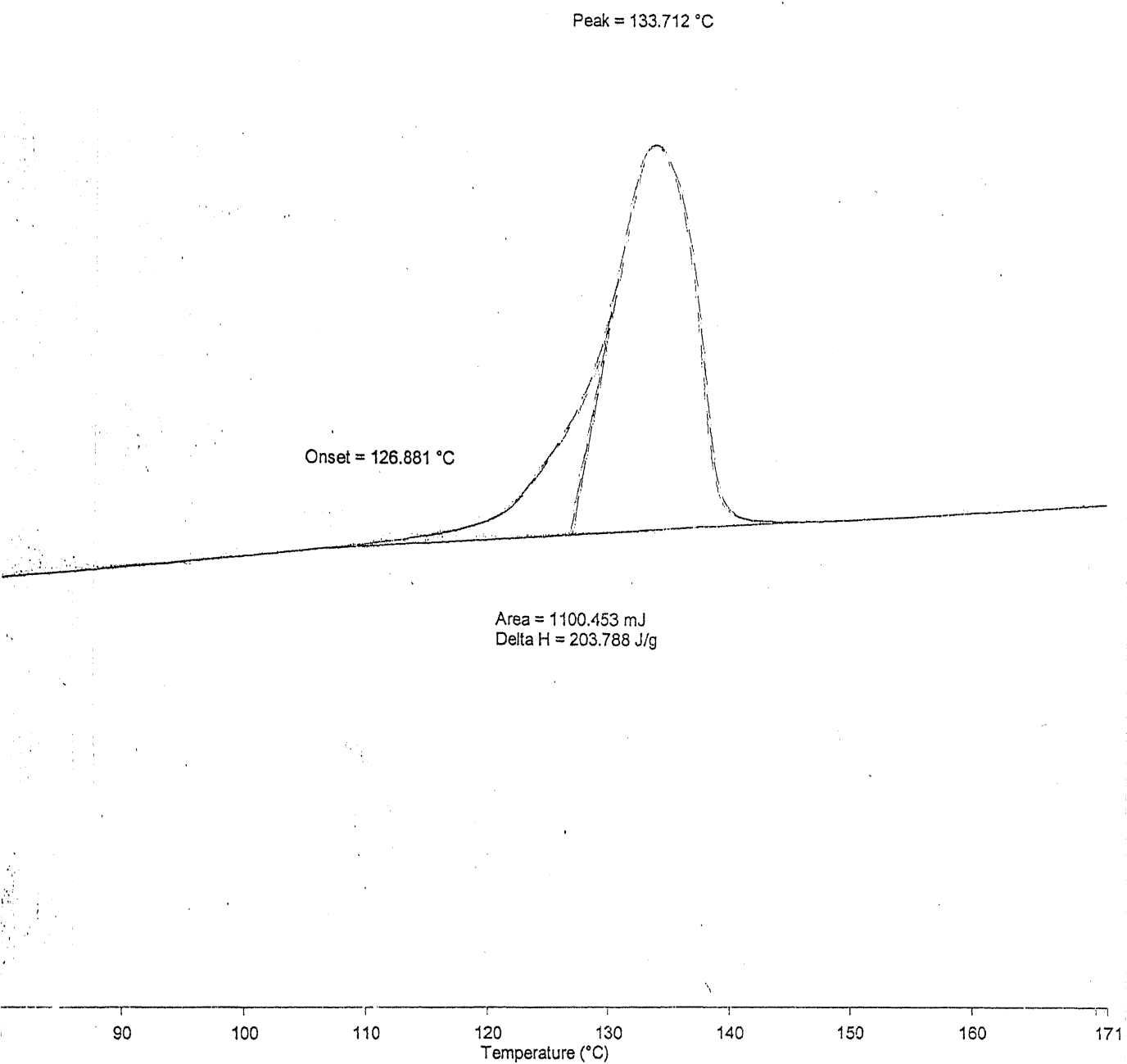| Iron	Abundance											
M	Ti				Zr				Hf			
X	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
$(\pi\text{-}C_5H_5)_2MX_2^+$	10	12	9	7	20	25	19	14	21	26	22	10
$(\pi\text{-}C_5H_5)_2MX^+$	4	18	24	37	5	9	28	45	5	4	20	38
$(\pi\text{-}C_5H_5)_2MX_2$	48	29	23	2	60	47	33	7S	61	50	34	14
$(\pi\text{-}C_5H_5)_2MX^+$	11	31	25	8	2	5	10	14	0	1	7	14
$(\pi\text{-}C_5H_5)_2M^+$	0	0	6	28	0	0	1	4	0	0	1	8
$(\pi\text{-}C_5H_5)M^+$	0	0	4	6	0	0	0	3	0	0	0	1
$C_3H_3MX_2^+$	4	2	0	0	8	7	4	5	10	14	11	4
$C_3H_3MX^+$	5	4	3	4	1	4	4	4	1	2	3	11
MX_2^+	17	2	5	5	4	3	1	1	2	3	2	0
M^+	1	2	1	3	0	0	0	3	0	0	0	0

Table A 9
Physical Properties of Compounds[3]

S.No.	Name	Formula	Molecular Weight, g/mol	Boiling Point @1atm, °K	Density of Liquid @ 20°C g/ml	Solubility in water @25°C,ppm
1	Benezene	C_6H_6	78.114	353	0.875	1,755
2	Toluene	C_7H_8	92.141	383	0.862	542.4
3.	o-Xylene	C_8H_{10}	106.167	1417	0.875	220.8
4.	Methanol	CH_3OH	32.04	337	0.785	Total
5.	Ethanol	C_2H_5OH	46.069	351	0.783	Total
6.	n-Haxane	C_6H_{14}	86.177	341	0.654	13.31
7.	Ethylene	C_2H_4	28.054	169	--	131.0
8.	Diethylether	$C_4H_{10}O$	74.0	308	0.71	Total
9.	Tetrahydrofuran	C_4H_8O	72.0	338	--	-
10.	Chloroform	$CHCl_3$	119.5	334	1.492	-
11.	Ethylbromide	C_2H_5Br	108.97	310	1.46	-
12.	Titaniumtetrachloride	$TiCl_4$	189.71	408	1.73	Reactive
13.	Triethylaluminum	$(C_2H_5)_3Al$	114.17	228	0.835	Reactive

[2] A.F. Reid J. Organometal. Chem. 329, 1964   [3] Physical properties of hydrocarbons, volume 1 and 2,

Peak = 133.712 °C

Onset = 126.881 °C

Area = 1100.453 mJ
Delta H = 203.788 J/g

Temperature (°C)

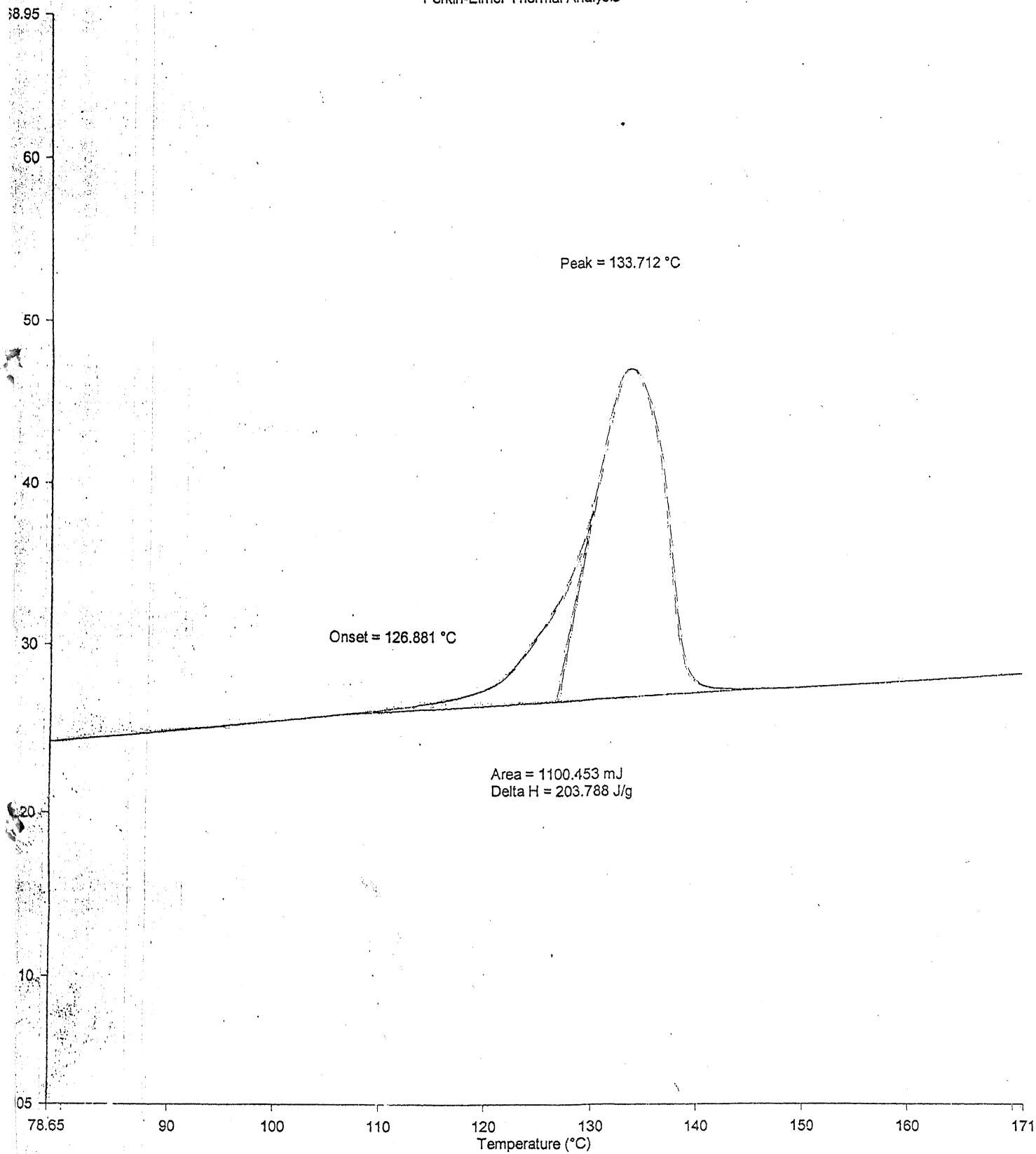90   100   110   120   130   140   150   160   171

9/23/02 4:03:06 PM

om 50.00°C to 200.00°C at 10.00°C/min

Filename: C:\PE\Pyris\Data\IIT-PV-III.dcd
Operator ID: MK
Sample ID: SAMPLE PV-III (Polyethylene)
Sample Weight: 5.400 mg
Comment: TEMP SCAN
                 (Sample from IIT,Kanpur)

Perkin-Elmer Thermal Analysis

Peak = 133.712 °C

Onset = 126.881 °C

Area = 1100.453 mJ
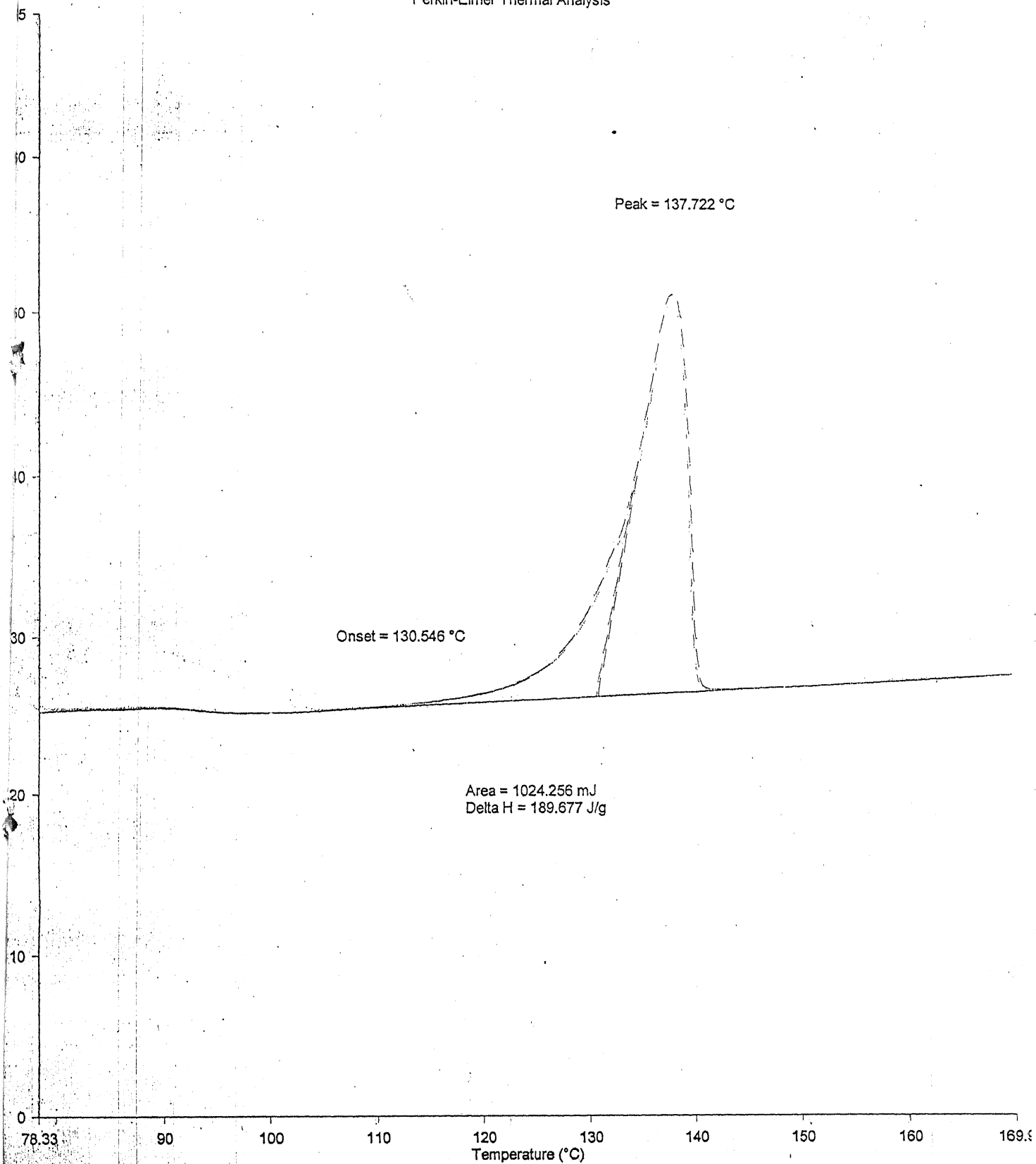Delta H = 203.788 J/g

Temperature (°C)

9/23/02 4:03:06 PM

at from 50.00°C to 200.00°C at 10.00°C/min

name: C:\PE\Pyris\Data\IIT-PV-IV.dcd
rator ID: MK
ple ID: SAMPLE PV-IV (Polyethylene)
ple Weight: 5.400 mg
ment: TEMP SCAN
(Sample from IIT,Kanpur)

Perkin-Elmer Thermal Analysis

Peak = 137.722 °C

Onset = 130.546 °C

Area = 1024.256 mJ
Delta H = 189.677 J/g

Temperature (°C)

9/23/02 3:59:46 PM

Heat from 50.00°C to 200.00°C at 10.00°C/min